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(54) Title: FORMULATIONS COMPRISING WATER-SOLUBLE GRANULATES

(57) Abstract: The present invention relates to formulations comprising water-soluble granulates of phthalocyanine compounds, to a process for the preparation thereof, and to the use thereof in washing agent and washing agent additive formulations.

FORMULATIONS COMPRISING WATER-SOLUBLE GRANULATES

The present invention relates to formulations comprising water-soluble non-encapsulated granulates of phthalocyanine compounds, to a process for the preparation thereof, and to the use thereof in washing agent and washing agent additive formulations.

The formulations according to the invention may be liquid, solid, paste-like or gel-like.

The formulations, especially washing agent compositions but also washing agent additives or additive concentrates, for example pre- and/or after-treatment agents, stain-removing salt, washing-power enhancers, fabric conditioners, bleaching agents, UV-protection enhancers etc., may be in any known and customary form, especially in the form of powders, (super-)compact powders, in the form of single- or multi-layer tablets (tabs), bars, blocks, sheets or pastes, or in the form of pastes, gels or liquids used in capsules or in pouches (sachets).

It is also possible for powders to be used in suitable sachets or pouches.

Water-soluble phthalocyanine compounds, especially zinc and aluminium phthalocyanine-sulfonates, are frequently used as photoactivators in washing agent preparations.

EP 333 270 describes solid microcapsules of phthalocyanine photoactivators, which comprise at least 38 % of an encapsulating material.

EP 959 123 describes granulates based on anionic dispersing agents in conjunction with a water-soluble organic polymer.

EP 323 407 describes encapsulated granules comprising an active ingredient.

EP 124 478 describes a process for the preparation of solid photoactivator preparations, which comprises passing a crude solution of the photoactivators through a modified membrane and subjecting the resulting concentrated aqueous solution to a gentle drying process.

EP 236 270 describes a process for the preparation of structures comprising an active substance and their use as speckles, having an average diameter of 0.5 – 1.0 mm.

However, owing to the fact that such photoactivators dissolve too slowly in water, problems often arise, especially when there is inadequate mixing of the washing liquor, because the coloured photoactivators stain the laundry.

It has now been found that the rate at which granules of phthalocyanine compounds dissolve in water can be improved further by a novel composition. This is achieved by the addition of at least one inorganic salt and/or at least one low-molecular-weight organic acid. Despite their high dissolution rate, such non-encapsulated granules, having a distribution of ingredients that is substantially homogeneous, have a high level of durability in non-ionic surfactants (NIO surfactants).

The present invention accordingly relates to formulations comprising at least one granulate containing

- a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound, based on the total weight of the granulate,
- b) from 10 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, based on the total weight of the granulate,
- c) from 15 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof, based on the total weight of the granulate,
- d) from 0 to 10 % by weight of at least one further additive, based on the total weight of the granulate, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate.

The sum of the percentages of components a) – e) by weight is always 100 %.

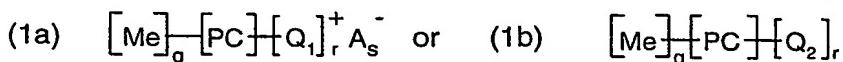
The formulation according to the invention may also comprise a mixture of granulates having different compositions and it is also possible for granulates not having a composition according to the invention to be used in admixture.

The granulates in the formulations according to the invention are not encapsulated and have a substantially homogeneous distribution of ingredients.

As the phthalocyanine compound for the granulates there come into consideration phthalocyanine complexes with di-, tri- or tetra-valent metals (complexes having a d⁰ or d¹⁰ configuration) as the central atom.

Such complexes are especially water-soluble Zn(II), Fe(II), Ca(II), Mg(II), Na(I), K(I), Al, Si(IV), P(V), Ti(IV), Ge(IV), Cr(VI), Ga(III), Zr(IV), In(III), Sn(IV) and Hf(VI) phthalocyanines, aluminium and zinc phthalocyanines being especially preferred.

The granulate of the formulation according to the invention advantageously comprises at least one phthalocyanine compound of formula



wherein

PC is the phthalocyanine ring system;

Me is Zn; Fe(II); Ca; Mg; Na; K; Al-Z₁; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV); In(III); Sn(IV) or Hf(VI);

Z₁ is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion;

q is 0, 1 or 2;

r is from 1 to 4;

Q₁ is a sulfo or carboxy group; or is a radical of formula

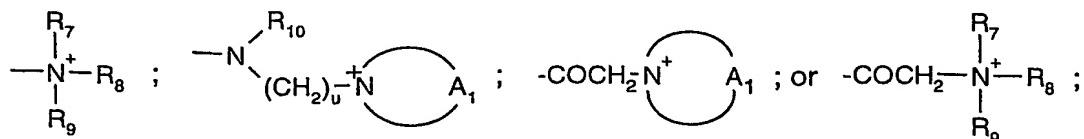


wherein

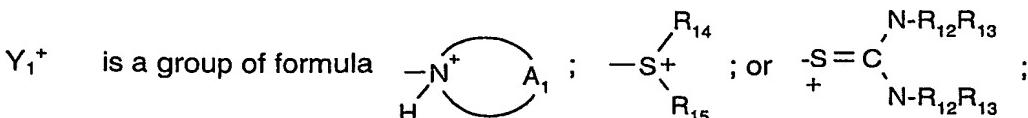
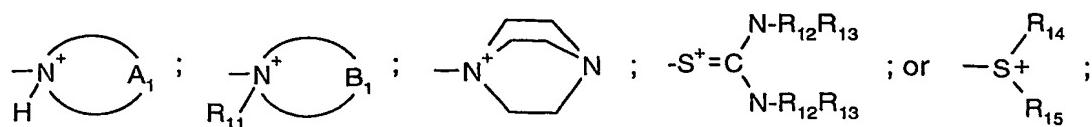
R₆ is branched or unbranched C₁-C₈alkylene; or 1,3- or 1,4-phenylene;

X₂ is -NH-; or -N-C₁-C₅alkyl-;

X₃⁺ is a group of formula



and, in the case where R₆ = C₁-C₈alkylene, may also be a group of formula



t is 0 or 1;

in which above formulae,

R₇ and R₈ are each independently of the other C₁-C₆alkyl;

R₉ is C₁-C₆alkyl; C₅-C₇cycloalkyl; or NR₁₁R₁₂;

R₁₀ and R₁₁ are each independently of the other C₁-C₅alkyl;

R₁₂ and R₁₃ are each independently of the other hydrogen or C₁-C₅alkyl;

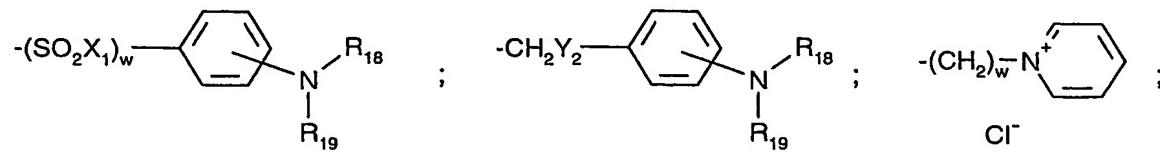
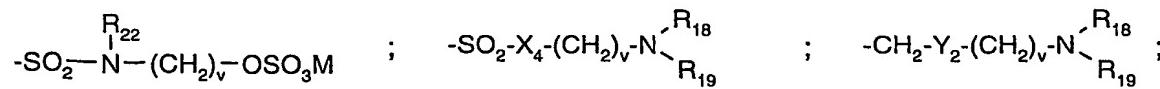
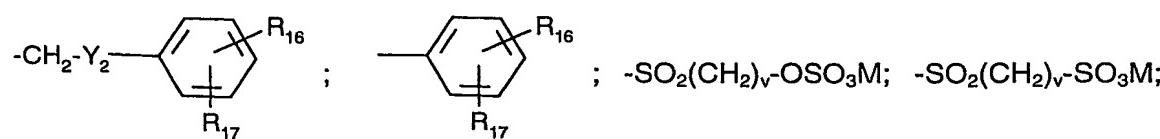
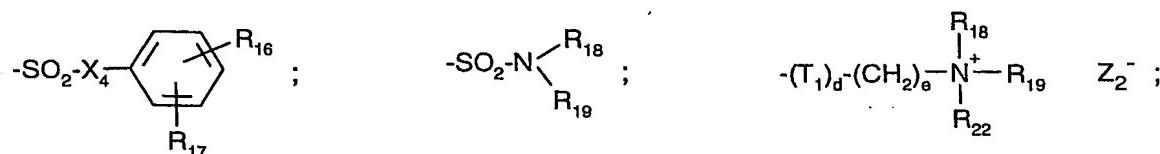
R₁₄ and R₁₅ are each independently of the other unsubstituted or hydroxy-, cyano-, carboxy-, C₁-C₆alkoxy-carbonyl-, C₁-C₆alkoxy-, phenyl-, naphthyl- or pyridyl-substituted C₁-C₆alkyl;

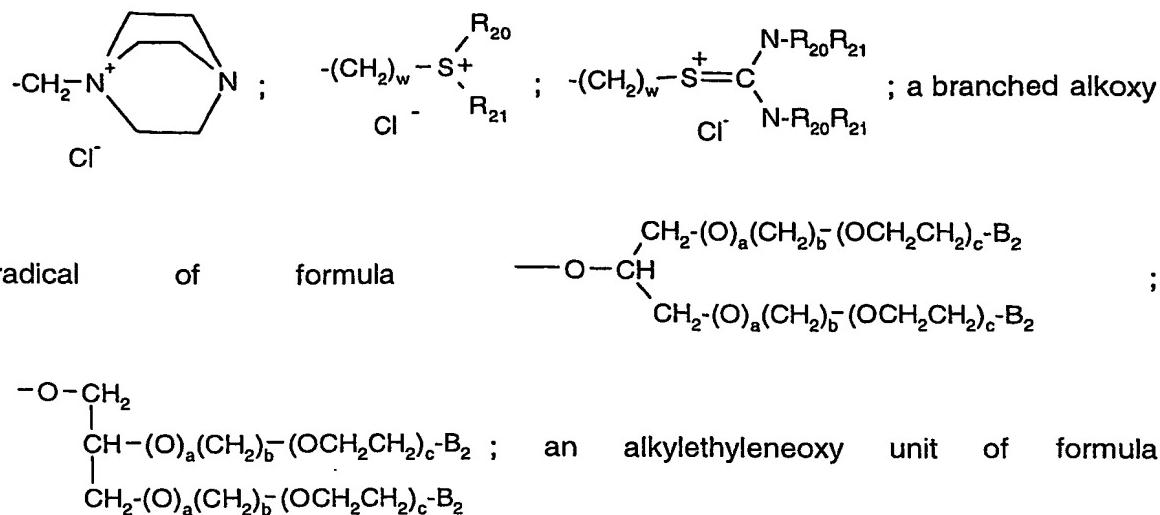
u is from 1 to 6;

A₁ is the balance of an aromatic 5- to 7-membered nitrogen heterocycle which may contain one or two further nitrogen atoms as ring members, and

B₁ is the balance of a saturated 5- to 7-membered nitrogen heterocycle which may contain 1 or 2 further nitrogen, oxygen and/or sulfur atoms as ring members;

Q₂ is hydroxy; C₁-C₂₂alkyl; branched C₃-C₂₂alkyl; C₂-C₂₂alkenyl; branched C₄-C₂₂alkenyl or a mixture thereof; C₁-C₂₂alkoxy; a sulfo or carboxy radical; a radical of formula





$-(\text{T}_1)_d-(\text{CH}_2)_b(\text{OCH}_2\text{CH}_2)_a\text{-B}_3$ or an ester of formula COOR_{23} ,

wherein

B_2 is hydrogen; hydroxy; $\text{C}_1\text{-C}_{30}$ alkyl; $\text{C}_1\text{-C}_{30}$ alkoxy; $-\text{CO}_2\text{H}$; $-\text{CH}_2\text{COOH}$; SO_3^-M_1 ; $-\text{OSO}_3^-\text{M}_1$; $-\text{PO}_3^{2-}\text{M}_1$; $-\text{OPO}_3^{2-}\text{M}_1$; or a mixture thereof;

B_3 is hydrogen; hydroxy; $-\text{COOH}$; $-\text{SO}_3^-\text{M}_1$; $-\text{OSO}_3^-\text{M}_1$; or $\text{C}_1\text{-C}_6$ alkoxy;

M_1 is a water-soluble cation;

T_1 is $-\text{O-}$; or $-\text{NH-}$;

X_1 and X_4 are each independently of the other $-\text{O-}$; $-\text{NH-}$; or $-\text{N-C}_1\text{-C}_5$ alkyl;

R_{16} and R_{17} are each independently of the other hydrogen; a sulfo group or a salt thereof; a carboxy group or a salt thereof, or a hydroxy group, at least one of the radicals R_{16} and R_{17} being a sulfo or carboxy group or a salt thereof,

Y_2 is $-\text{O-}$; $-\text{S-}$; $-\text{NH-}$ or $-\text{N-C}_1\text{-C}_5$ alkyl;

R_{18} and R_{19} are each independently of the other hydrogen; $\text{C}_1\text{-C}_6$ alkyl; hydroxy- $\text{C}_1\text{-C}_6$ alkyl; cyano- $\text{C}_1\text{-C}_6$ alkyl; sulfo- $\text{C}_1\text{-C}_6$ alkyl; carboxy- or halo- $\text{C}_1\text{-C}_6$ alkyl; unsubstituted or halo-, $\text{C}_1\text{-C}_4$ alkyl-, $\text{C}_1\text{-C}_4$ alkoxy-, sulfo- or carboxy-substituted phenyl; or R_{18} and R_{19} , together with the nitrogen atom to which they are bonded, are a saturated 5- or 6-membered heterocyclic ring which may additionally contain a further nitrogen or oxygen atom as ring member;

R_{20} and R_{21} are each independently of the other a $\text{C}_1\text{-C}_6$ alkyl or aryl- $\text{C}_1\text{-C}_6$ alkyl radical;

R_{22} is hydrogen; or unsubstituted or halo-, hydroxy-, cyano-, phenyl-, carboxy-, $\text{C}_1\text{-C}_6$ -alkoxy-carbonyl- or $\text{C}_1\text{-C}_6$ alkoxy-substituted $\text{C}_1\text{-C}_6$ alkyl;

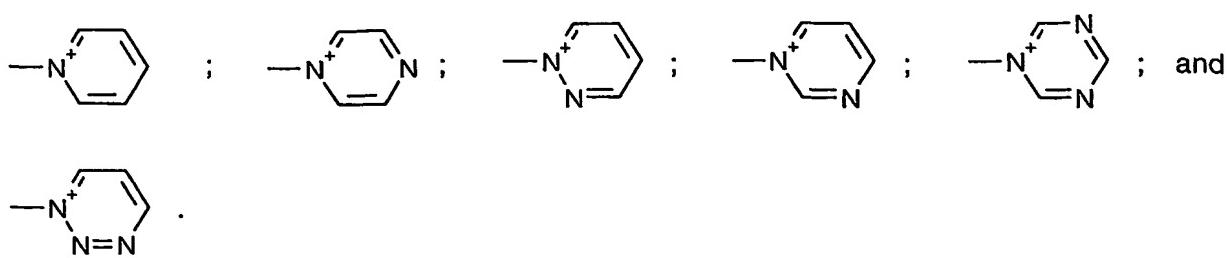
R_{23} is $\text{C}_1\text{-C}_{22}$ alkyl; branched $\text{C}_4\text{-C}_{22}$ alkyl; $\text{C}_1\text{-C}_{22}$ alkenyl or branched $\text{C}_4\text{-C}_{22}$ alkenyl; $\text{C}_3\text{-C}_{22}$ -glycol; $\text{C}_1\text{-C}_{22}$ alkoxy; branched $\text{C}_4\text{-C}_{22}$ alkoxy; or a mixture thereof;

M is hydrogen; or an alkali metal ion or ammonium ion,
 Z_2^- is a chlorine ion, bromine ion, alkylsulfate ion or aralkylsulfate ion;
a is 0 or 1;
b is from 0 to 6;
c is from 0 to 100;
d is 0 or 1;
e is from 0 to 22;
v is an integer from 2 to 12;
w is 0 or 1; and
 A^- is an organic or inorganic anion,
and
s in the case of monovalent anions A^- is equal to r and in the case of polyvalent anions is $\leq r$, it being necessary for A_s^- to balance the positive charge; and when $r \neq 1$, the radicals Q_1 may be identical or different,
and wherein the phthalocyanine ring system may also contain further solubility-imparting groups.

The number of substituents Q_1 and Q_2 in formula (1a) and in formula (1b), respectively, which substituents may be identical or different, is from 1 to 8 and, as is customary with phthalocyanines, the number need not be a whole number (degree of substitution). If other, non-cationic substituents are also present, the sum of the latter and the cationic substituents is from 1 to 4. The minimum number of substituents that need to be present in the molecule is governed by the water-solubility of the resulting molecule. An adequate solubility is achieved when the amount of phthalocyanine compound that dissolves is sufficient to cause photodynamically catalysed oxidation on the fibres. A solubility as low as 0.01 mg/l may be sufficient, but generally a solubility of from 0.001 to 1 g/l is expedient.

Halogen is fluorine, bromine or, especially, chlorine.

As groups $-N^+ A_1$, there come into consideration especially:



Preference is given to the group

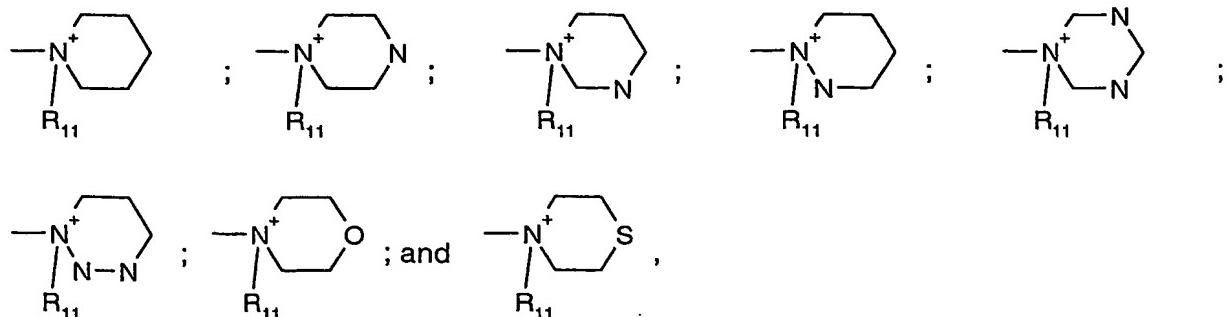
As heterocyclic rings in the group there likewise come into consideration

the groups mentioned above, but with the bond to the remaining substituents being effected by way of a carbon atom.

In all substituents, phenyl, naphthyl and aromatic hetero rings may be substituted by one or two further radicals, for example by C₁-C₆alkyl, C₁-C₆alkoxy, halogen, carboxy, C₁-C₆alkoxy-carbonyl, hydroxy, amino, cyano, sulfo, sulfonamido etc..

Preference is given to a substituent from the group C₁-C₆alkyl, C₁-C₆alkoxy, halogen, carboxy, C₁-C₆alkoxy-carbonyl and hydroxy.

As the group there come into consideration especially:



R₁₁ being as defined above, especially CH₃ or CH₂CH₃.

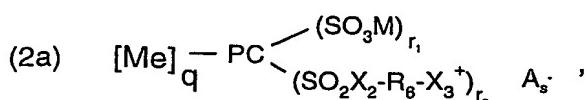
All above-mentioned nitrogen heterocycles may, in addition, be substituted by alkyl groups, either at a carbon atom or at a further nitrogen atom located in the ring, with preference being given to a methyl group as the alkyl group.

A_s^- in formula (1a) denotes, as counterion to the positive charge of the remainder of the molecule, any desired anion. It is generally introduced in the process of manufacture (quaternisation), in which case it is preferably a halogen ion, an alkylsulfate ion or an arylsulfate ion. Among the arylsulfate ions mention should be made of the phenylsulfonate, p-tolylsulfonate and p-chlorophenylsulfonate ions. It is also possible, however, for any other anion to function as the anion, since the anions can readily be interchanged in known manner; accordingly, A_s^- may also be a sulfate, sulfite, carbonate, phosphate, nitrate, acetate, oxalate, citrate or lactate ion or another anion of an organic carboxylic acid. In the case of monovalent anions, the index s is equal to r. In the case of polyvalent anions, s assumes a value $\leq r$ but must be such, depending on the conditions, that it exactly balances the positive charge of the remainder of the molecule.

C_1-C_6 Alkyl and C_1-C_6 alkoxy are straight-chain or branched alkyl and alkoxy radicals, respectively, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, amyl, isoamyl, tert-amyl or hexyl, and methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy, amyloxy, isoamyloxy, tert-amyloxy or hexyloxy, respectively.

C_2-C_{22} Alkenyl denotes, for example, allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobut enyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododec enyl, n-dodec-2-enyl or n-octadec-4-enyl.

Preferred phthalocyanine compounds of formula (1a) of the granulates correspond to formula



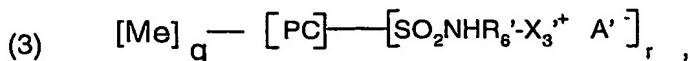
wherein

Me, q, PC, X_2 , X_3 and R_6 are as defined for formula (1a),

M is hydrogen; or an alkali metal ion, ammonium ion or amine salt ion;

and the sum of the numbers r_1 and r_2 is from 1 to 4, and

A_s^- exactly balances the positive charge of the remainder of the molecule, and especially to formula

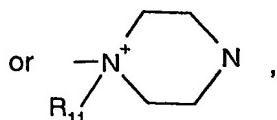
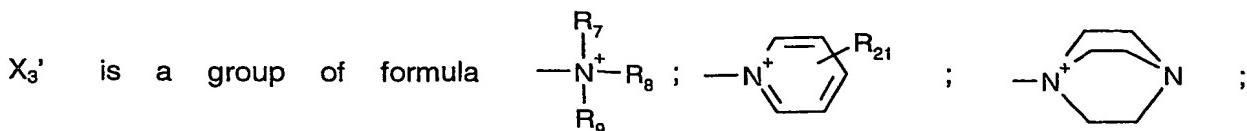


wherein

Me, q and PC are as defined for formula (1a),

R'_6 is C₂-C₆alkylene;

r is a number from 1 to 4;



wherein

R₇ and R₈ are each independently of the other unsubstituted or hydroxy-, cyano-, halo- or phenyl-substituted C₁-C₄alkyl;

R₉ is R₇; cyclohexyl or amino;

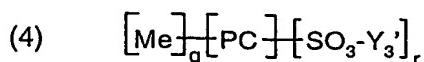
R₁₁ is C₁-C₄alkyl;

R₂₁ is C₁-C₄alkyl; C₁-C₄alkoxy; halogen; carboxy; C₁-C₄alkoxy-carbonyl or hydroxy; and

A'⁻ is a halide ion, alkylsulfate ion or arylsulfate ion;

it being possible for the radicals -SO₂NHR'_6-X₃⁺A'⁻ to be identical or different.

Further phthalocyanine compounds that can be used in the granulate of the formulations according to the invention correspond to formula



wherein

PC is the phthalocyanine ring system;

Me is Zn; Fe(II); Ca; Mg; Na; K; Al-Z₁; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV); In(III); Sn(IV) or Hf(VI);

Z₁ is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion;

q is 0; 1; or 2;

Y₃' is hydrogen; or an alkali metal ion or ammonium ion; and

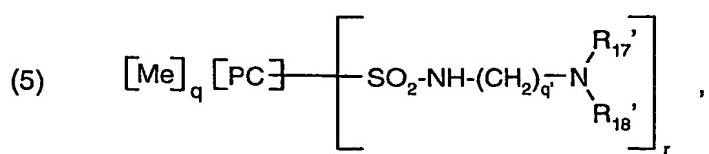
r is any number from 1 to 4.

Of those, very special preference is given to phthalocyanine compounds of formula (4) wherein

Me is Zn or Al-Z₁; and

Z₁ is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion.

Further phthalocyanine compounds of interest that can be used in the granulate of the formulations according to the invention correspond to formula



wherein

PC, Me and q are as defined for formula (4);

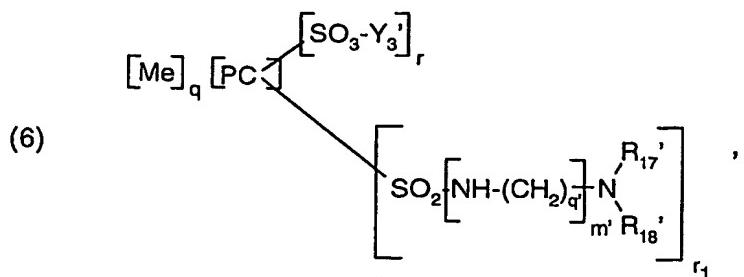
R₁₇' and R₁₈' are each independently of the other hydrogen; phenyl; sulfophenyl; carboxyphenyl; C₁-C₆alkyl; hydroxy-C₁-C₆alkyl; cyano-C₁-C₆alkyl; sulfo-C₁-C₆alkyl; carboxy-C₁-C₆alkyl or halo-C₁-C₆alkyl or, together with the nitrogen atom, form a morpholine ring;

q' is an integer from 2 to 6; and

r is a number from 1 to 4;

it being possible, when r > 1, for the radicals $-\text{SO}_2\text{-NH-(CH}_2\text{)}_{q'}\text{-N} \begin{array}{c} \text{R}_{17}' \\ | \\ \text{R}_{18}' \end{array}$ present in the molecule to be identical or different.

Further phthalocyanine compounds of interest that can be used in the granulate of the formulations according to the invention correspond to formula



wherein

PC, Me and q are as defined for formula (4).

Y_3^+ is hydrogen; or an alkali metal ion or ammonium ion

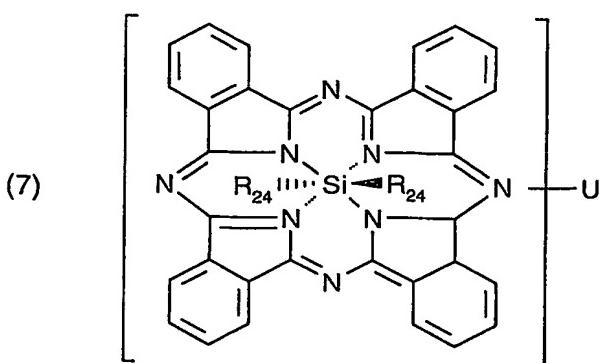
q' is an integer from 2 to 6.

R_{17}' and R_{18}' are each independently of the other hydrogen; phenyl; sulfophenyl; carboxyphenyl; C_1 - C_6 alkyl; hydroxy- C_1 - C_6 alkyl; cyano- C_1 - C_6 alkyl; sulfo- C_1 - C_6 alkyl; carboxy- C_1 - C_6 alkyl or halo- C_1 - C_6 alkyl or, together with the nitrogen atom, form a morpholine ring.

m' is 0 or 1; and

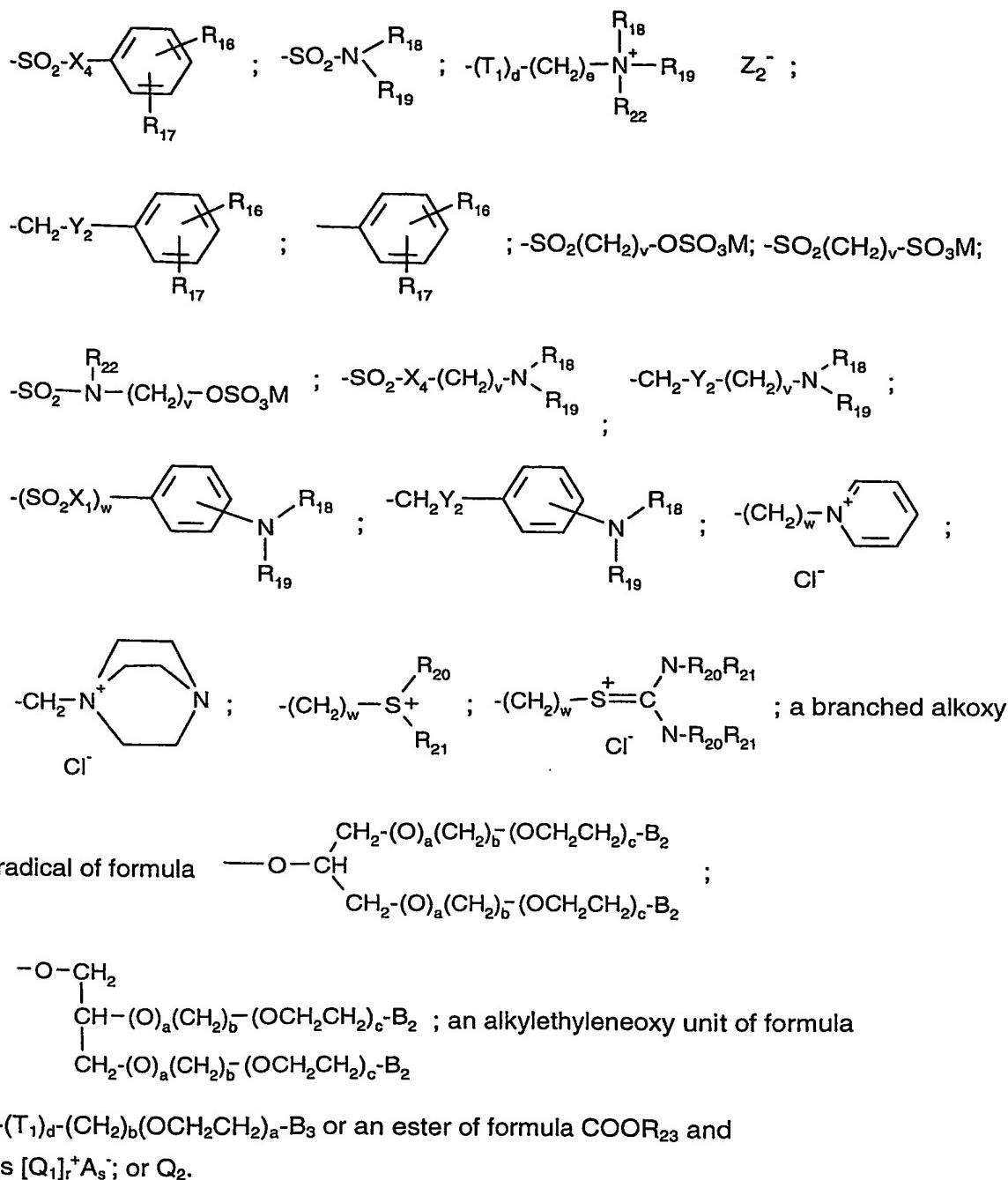
r and r_1 are each independently of the other any number from 0.5 to 3.5, the sum $r + r_1$ being a minimum of 1 and a maximum of 4.

Where the central atom Me in the phthalocyanine ring is Si(IV), the phthalocyanines used in the granulate of the formulations according to the invention may also contain, in addition to the substituents on the phenyl nucleus of the phthalocyanine ring, axial substituents (= R₂₄). Such phthalocyanines correspond, for example, to formula



wherein

R₂₄ is hydroxy; C₁-C₂₂alkyl; branched C₄-C₂₂alkyl; C₁-C₂₂alkenyl; branched C₄-C₂₂alkenyl or a mixture thereof; C₁-C₂₂alkoxy; a sulfo or carboxy radical; a radical of formula



$\text{R}_{16}, \text{R}_{17}, \text{R}_{18}, \text{R}_{19}, \text{R}_{20}, \text{R}_{21}, \text{R}_{22}, \text{R}_{23}, \text{B}_2, \text{B}_3, \text{M}, \text{Q}_1, \text{Q}_2, \text{A}_s, \text{T}_1, \text{X}_1, \text{X}_4, \text{Y}_2, \text{Z}_2^-, \text{a}, \text{b}, \text{c}, \text{d}, \text{e}, \text{r}, \text{v}$
and w therein being as defined for formulae (1a) and (1b).

Especially preferred phthalocyanine compounds are such compounds as are commercially available and used in washing agent compositions. Usually, the anionic phthalocyanine compounds are in the form of alkali metal salts, especially sodium salts.

The granulates in the formulations according to the invention contain from 2 to 50 % by weight, preferably from 4 to 30 % by weight, especially from 5 to 20 % by weight, of at least one phthalocyanine compound, based on the total weight of the granulate.

The granulates in the formulations according to the invention contain from 10 to 60 % by weight, preferably from 12 to 60 % by weight, especially from 12 to 55 % by weight, of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, based on the total weight of the granulate.

Such anionic dispersing agents and also the water-soluble organic polymers, which may also have dispersing properties, are described hereinbelow.

Anionic dispersing agents:

The anionic dispersing agents used are, for example, the commercially available water-soluble anionic dispersing agents for dyes, pigments etc..

The following products, especially, come into consideration: condensation products of aromatic sulfonic acids and formaldehyde, condensation products of aromatic sulfonic acids with unsubstituted or chlorinated biphenyls or biphenyl oxides and optionally formaldehyde, (mono-/di-)alkylnaphthalenesulfonates, sodium salts of polymerised organic sulfonic acids, sodium salts of polymerised alkylbenzenesulfonic acids, alkylarylsulfonates, sodium salts of alkyl polyglycol ether sulfates, polyalkylated polynuclear arylsulfonates, methylene-linked condensation products of arylsulfonic acids and hydroxyarylsulfonic acids, sodium salts of dialkylsulfosuccinic acids, sodium salts of alkyl diglycol ether sulfates, sodium salts of polynaphthalene-methanesulfonates, ligno- or oxyligno-sulfonates or heterocyclic polysulfonic acids.

Especially suitable anionic dispersing agents are condensation products of naphthalene-sulfonic acids with formaldehyde, sodium salts of polymerised organic sulfonic acids, (mono-/di-)alkylnaphthalenesulfonates, polyalkylated polynuclear arylsulfonates, sodium salts of polymerised alkylbenzenesulfonic acid, lignosulfonates, oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl.

Instead of or in addition to the dispersing agent or agents, the granulates according to the invention may comprise a water-soluble organic polymer, which may also have dispersing properties. Such polymers may be used singly or as mixtures of two or more polymers. As water-soluble polymers (which may, but need not, have film-forming properties), there come into consideration, for example, gelatins, polyacrylates, polymethacrylates, copolymers of ethyl acrylate, methyl methacrylate and methacrylic acid (ammonium salt), polyvinylpyrrolidones, vinylpyrrolidones, vinyl acetates, copolymers of vinylpyrrolidone with long-chain olefins, poly(vinylpyrrolidone/dimethylaminoethyl methacrylates), copolymers of vinylpyrrolidone/dimethylaminopropyl methacrylamides, copolymers of vinylpyrrolidone/dimethylaminopropyl acrylamides, quaternised copolymers of vinylpyrrolidones and dimethylaminoethyl methacrylates, terpolymers of vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of vinylpyrrolidone and methacrylamidopropyltrimethylammonium chloride, terpolymers of caprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of styrene and acrylic acid, polycarboxylic acids, polyacrylamides, carboxymethyl cellulose, hydroxymethyl cellulose, polyvinyl alcohols, hydrolysed and non-hydrolysed polyvinyl acetate, copolymers of maleic acid with unsaturated hydrocarbons and also mixed polymerisation products of the mentioned polymers. Further suitable substances are polyethylene glycol (MW = 4000 – 20 000), copolymers of ethylene oxide with propylene oxide (MW > 3500), condensation products (block polymerisation products) of alkylene oxide, especially propylene oxide, copolymers of vinylpyrrolidone with vinyl acetate, ethylene oxide-propylene oxide addition products with diamines, especially ethylenediamine, polystyrenesulfonic acid, polyethylene-sulfonic acid, copolymers of acrylic acid with sulfonated styrenes, gum arabic, hydroxypropyl methylcellulose, sodium carboxymethyl cellulose, hydroxypropyl methylcellulose phthalate, maltodextrin, starch, sucrose, lactose, enzymatically modified and subsequently hydrated sugars, as are obtainable under the name "Isomalt", cane sugar, polyaspartic acid and tragacanth.

Among those water-soluble organic polymers, special preference is given to carboxymethyl cellulose, polyacrylamides, polyvinyl alcohols, polyvinylpyrrolidones, gelatins, hydrolysed polyvinyl acetates, copolymers of vinylpyrrolidone and vinyl acetate, maltodextrins, polyaspartic acid and also polyacrylates and polymethacrylates.

The granulates in the formulations according to the invention contain from 15 to 75 % by weight, preferably from 20 to 75 % by weight, especially from 25 to 70 % by weight, of at

least one inorganic salt and/or at least one low-molecular-weight organic acid and/or a salt thereof.

The mentioned components are described in detail hereinbelow:

Inorganic salts:

For use as inorganic salts there come into consideration carbonates, hydrogen carbonates, phosphates, polyphosphates, sulfates, silicates, sulfites, borates, halides and pyrophosphates, preferably in the form of alkali metal salts. Preference is given to water-soluble salts such as, for example, alkali metal chlorides, alkali phosphates, alkali carbonates, alkali polyphosphates and alkali sulfates and water-soluble salts used in washing agent and/or washing agent additive formulations.

Low-molecular-weight organic acids and salts thereof:

There come into consideration as low-molecular-weight acids, for example, mono- or polycarboxylic acids. Of special interest are aliphatic carboxylic acids, especially those having a total number of from 1 to 12 carbon atoms. Preferred acids are aliphatic C₁-C₁₂mono- or -poly-carboxylic acids, the monocarboxylic acids being especially those having at least 3 carbon atoms in total. As substituents of the carboxylic acids there come into consideration, for example, hydroxy and amino, especially hydroxy. Special preference is given to aliphatic C₂-C₁₂polycarboxylic acids, especially aliphatic C₂-C₆polycarboxylic acids. Very special preference is given to hydroxy-substituted aliphatic C₂-C₆polycarboxylic acids. These compounds may be used in the form of the free acid or a salt, especially an alkali salt.

There may also be used aminopolycarboxylates (e.g. sodium ethylenediaminetetraacetate), phytates, phosphonates, aminopolyphosphonates (e.g. sodium ethylenediaminetetraphosphonate), aminoalkylenepoly(alkylenephosphonates), polyphosphonates, polycarboxylates or water-soluble polysiloxanes.

As examples of low-molecular-weight organic acids and salts thereof there may be mentioned oxalic acid, tartaric acid, acetic acid, propionic acid, succinic acid, maleic acid, citric acid, formic acid, gluconic acid, p-toluenesulfonic acid, terephthalic acid, benzoic acid, phthalic acid, acrylic acid and polyacrylic acid.

The granulates in the formulations according to the invention may comprise further additives, for example wetting agents, disintegrants such as, for example, powdered or fibrous cellulose, microcrystalline cellulose, fillers such as, for example, dextrin, water-insoluble or water-soluble dyes or pigments, and also dissolution accelerators and optical brighteners. Aluminium silicates such as zeolites, and also compounds such as talc, kaolin, TiO₂, SiO₂ or magnesium trisilicate may also be used in small amounts. Such additives are present in an amount of from 0 to 10 % by weight, preferably from 0 to 5 % by weight, based on the total weight of the granulates.

As especially preferred additives, special emphasis is to be given to powdered or fibrous cellulose and to aluminium silicates. These are present in an amount of from 0 to 10 % by weight, preferably from 0 to 5 % by weight, based on the total weight of the granulates.

The granulates in the formulations according to the invention may contain from 3 to 15 % water by weight, based on the total weight of the granulate.

A preferred formulation according to the invention comprises at least one granulate consisting of

- a) from 4 to 30 % by weight of at least one water-soluble phthalocyanine compound,
- b) from 12 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer,
- c) from 20 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof,
- d) from 0 to 5 % by weight of at least one further additive, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate.

A formulation according to the invention to which greater preference is given comprises at least one granulate consisting of

- a) from 5 to 20 % by weight of at least one water-soluble phthalocyanine compound,
- b) from 12 to 55 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer,
- c) from 25 to 70 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof,
- d) from 0 to 5 % by weight of at least one zeolite compound and, where appropriate, further additives, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate.

A likewise preferred formulation according to the invention comprises at least one granulate consisting of

- a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound of formula (2a), (3), (4), (5), (6) and/or (7) defined above,
- b) from 10 to 60 % by weight of at least one anionic dispersing agent from the group consisting of condensation products of naphthalene-sulfonic acid with formaldehyde; sodium salts of polymerised organic sulfonic acids; (mono-/di-)alkyl-naphthalenesulfonates; polyalkylated polynuclear aryl-sulfonates; sodium salts of polymerised alkylbenzene-sulfonic acids; lignosulfonates; oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl;
and/or at least one water-soluble organic polymer from the group consisting of carboxymethyl cellulose; polyacrylamides; polyvinyl alcohols; polyvinylpyrrolidones; gelatins; hydrolysed polyvinyl acetates; copolymers of vinylpyrrolidone and vinyl acetate; maltodextrins; polyaspartic acid; polyacrylates and polymethacrylates, and
- c) from 15 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof from the group consisting of carbonates; hydrogen carbonates; phosphates; polyphosphates; sulfates; silicates; sulfites; borates; halides; pyrophosphates; aliphatic carboxylic acids having a total number of from 1 to 12 carbon atoms, which are unsubstituted or substituted by hydroxy and/or by amino; aminopolycarboxylates; phytates; phosphonates; aminopolyphosphonates; aminoalkylene-poly(alkylenephosphonates); polyphosphonates; polycarboxylates; water-soluble polysiloxanes; and water-soluble salts that are used in washing agent and/or washing agent additive formulations, and
- d) from 0 to 10 % by weight of at least one further additive from the group consisting of wetting agents; disintegrants; fillers; water-insoluble or

water-soluble dyes or pigments; dissolution accelerators; optical brighteners; aluminium silicates; talc; kaolin; TiO₂, SiO₂; and magnesium trisilicate, and

- e) from 3 to 15 % by weight water, based on the total weight of the granulate.

The granulates in the formulations according to the invention preferably have an average particle size of < 500 µm. Greater preference is given to the particle size of the granulates being from 40 to 400 µm.

The formulations according to the invention can, depending on the composition of the granulate according to the invention, be used as such, as an additive in other formulations or in combination with another formulation. Preference is given to use of the formulations according to the invention in a washing agent composition or in a washing agent additive, for example a pre- and/or after-treatment agent, stain-removing salt, washing-power enhancer, fabric conditioner, bleaching agent or UV-protection enhancer.

The formulations according to the invention are used especially as an additive in a washing agent formulation. Such a washing agent formulation may be in solid, liquid, gel-like or paste-like form, for example in the form of a liquid, non-aqueous washing agent composition containing not more than 5 % by weight, preferably from 0 to 1 % by weight, water and based on a suspension of a builder substance in a non-ionic surfactant, for example as described in GB-A-2 158 454.

The formulations according to the invention may also be in the form of powders or (super-)compact powders, in the form of single- or multi-layer tablets (tabs), in the form of washing agent bars, washing agent blocks, washing agent sheets, washing agent pastes or washing agent gels, or in the form of powders, pastes, gels or liquids used in capsules or in pouches (sachets).

However, the washing agent compositions are preferably in the form of non-aqueous formulations, powders, tabs or granules.

The present invention accordingly relates also to washing agent formulations containing

- I) from 5 to 70 % A) of at least one anionic surfactant and/or B) at least one non-ionic surfactant, based on the total weight of the washing agent formulation,

- II) from 5 to 60 % C) of at least one builder substance, based on the total weight of the washing agent formulation,
- III) from 0 to 30 % D) of at least one peroxide and, optionally, at least one activator, based on the total weight of the washing agent formulation, and
- IV) from 0.001 to 1 % E) of at least one granulate which contains
 - a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound, based on the total weight of the granulate,
 - b) from 10 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, based on the total weight of the granulate,
 - c) from 15 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof, based on the total weight of the granulate,
 - d) from 0 to 10 % by weight of at least one further additive, based on the total weight of the granulate, and
 - e) from 3 to 15 % by weight water, based on the total weight of the granulate,
- V) from 0 to 60 % F) of at least one further additive, and
- VI) from 0 to 5 % G) water.

The sum of the percentages by weight of components I) – VI) in a formulation is always 100 %.

All the preferences mentioned hereinbefore apply to the granulate E).

The anionic surfactant A) may be, for example, a sulfate, sulfonate or carboxylate surfactant or a mixture of those surfactants. Preferred sulfates are those having from 12 to 22 carbon atoms in the alkyl radical, where appropriate in combination with alkyl ethoxysulfates having from 10 to 20 carbon atoms in the alkyl radical. Preferred sulfonates are, for example, alkylbenzenesulfonates having from 9 to 15 carbon atoms in the alkyl radical and/or alkylnaphthalenesulfonates having from 6 to 16 carbon atoms in the alkyl radical. The cation in the anionic surfactant is preferably an alkali metal cation, especially sodium. Preferred carboxylates are alkali metal sarcosinates of the formula R-CO-N(R¹)-CH₂COOM¹, wherein R is alkyl or alkenyl having from 8 to 18 carbon atoms in the alkyl or alkenyl radical, R¹ is C₁-C₄alkyl and M¹ is an alkali metal.

The non-ionic surfactant B) may be, for example, a condensation product of from 3 to 8 mols of ethylene oxide with 1 mol of primary alcohol containing from 9 to 15 carbon atoms.

There come into consideration as builder substance C), for example, alkali metal phosphates, especially tripolyphosphates, carbonates or hydrogen carbonates, especially the sodium salts, silicates, aluminium silicates, polycarboxylates, polycarboxylic acids, organic phosphonates, aminoalkylenepoly(alkylenephosphonates) or mixtures of those compounds. Especially suitable silicates are sodium salts of crystalline silicates having layered structures of the formula $\text{NaHSi}_t\text{O}_{2t+1} \cdot p\text{H}_2\text{O}$ or $\text{Na}_2\text{Si}_t\text{O}_{2t+1} \cdot p\text{H}_2\text{O}$, wherein t is a number from 1.9 to 4 and p is a number from 0 to 20. Among the aluminium silicates, preference is given to those obtainable commercially under the names zeolite A, B, X and HS, and also to mixtures comprising two or more of those components.

Among the polycarboxylates, preference is given to polyhydroxycarboxylates, especially citrates, and acrylates and also copolymers thereof with maleic anhydride. Preferred polycarboxylic acids are nitrilotriacetic acid, ethylenediaminetetraacetic acid and ethylenediamine disuccinate either in racemic form or in the enantiomerically pure S,S form. Phosphonates and aminoalkylenepoly(alkylenephosphonates) that are especially suitable are alkali metal salts of 1-hydroxyethane-1,1-diphosphonic acid, nitrilotris(methylene-phosphonic acid), ethylenediaminetetramethylenephosphonic acid and diethylenetriamine-pentamethylenephosphonic acid.

There come into consideration as the peroxide component D), for example, the organic and inorganic peroxides known in the literature and available commercially that bleach textile materials at conventional washing temperatures, for example at from 10 to 95°C. The organic peroxides are, for example, mono- or poly-peroxides, especially organic peracids or salts thereof, such as phthalimidoperoxyacrylic acid, peroxybenzoic acid, diperoxydodecanoic diacid, diperoxynonanoic diacid, diperoxydecanoic diacid, diperoxyphthalic acid or salts thereof. Preferably, however, inorganic peroxides are used, such as, for example, persulfates, perborates, percarbonates and/or persilicates. It will be understood that mixtures of inorganic and/or organic peroxides can also be used. The peroxides may be in a variety of crystalline forms and have different water contents, and they may also be used together with other inorganic or organic compounds in order to improve their storage

stability. The peroxides are added to the washing agent composition preferably by mixing the components, for example using a screw metering system and/or a fluidised bed mixer.

The washing agent compositions may comprise, in addition to the combination according to the invention, one or more optical brighteners, for example from the class bis-triazinylaminostilbenedisulfonic acid, bis-triazolylstilbenedisulfonic acid, bis-styrylbiphenyl and bis-benzofuranyl biphenyl, a bis-benzoxaryl derivative, bis-benzimidazolyl derivative, coumarin derivative or a pyrazoline derivative.

The washing agent compositions may also comprise suspending agents for dirt, e.g. sodium carboxymethyl cellulose, pH regulators, e.g. alkali metal or alkaline earth metal silicates, foam regulators, e.g. soap, salts for regulating the spray-drying and the granulating properties, e.g. sodium sulfate, fragrances and, optionally, antistatic agents and fabric conditioners, enzymes, such as amylase, bleaching agents, pigments and/or toning agents. It will be understood that such constituents must be stable towards the bleaching agent used.

Further preferred additives to the washing agent compositions according to the invention are polymers which, during the washing of textiles, prevent staining caused by dyes in the washing liquor which have been released from the textiles under the washing conditions. Such polymers are preferably polyvinylpyrrolidones which, where appropriate, have been modified by the incorporation of anionic or cationic substituents, especially those polyvinylpyrrolidones having a molecular weight in the range from 5000 to 60 000, more especially from 10 000 to 50 000. Such polymers are preferably used in an amount of from 0.05 to 5 % by weight, especially from 0.2 to 1.7 % by weight, based on the total weight of the washing agent composition.

In addition, the washing agent compositions according to the invention may also comprise so-called perborate activators, such as, for example, TAED or TAGU. Preference is given to TAED, which is preferably used in an amount of from 0.05 to 5 % by weight, especially from 0.2 to 1.7 % by weight, based on the total weight of the washing agent composition.

The percentages of components I) to VI) in the washing agent formulations hereinbelow are in all cases based on the total weight of the washing agent formulation.

A preferred washing agent formulation according to the invention consists of

- I) from 5 to 70 % A) of at least one anionic surfactant from the group consisting of alkylbenzenesulfonates having from 9 to 15 carbon atoms in the alkyl radical; alkyl-naphthalenesulfonates having from 6 to 16 carbon atoms in the alkyl radical; and alkali metal sarcosinates of the formula R-CO-N(R₁)-CH₂COOM₁,
wherein R is alkyl or alkenyl having from 8 to 18 carbon atoms in the alkyl or alkenyl radical,
R₁ is C₁-C₄alkyl and
M₁ is an alkali metal and/or
- B) at least one non-ionic surfactant from the group consisting of condensation products of from 3 to 8 mols of ethylene oxide with 1 mol of primary alcohol containing from 9 to 15 carbon atoms,
- II) from 5 to 60 % C) of a builder substance from the group consisting of alkali metal phosphates; carbonates; hydrogen carbonates; silicates; aluminium silicates; polycarboxylates; polycarboxylic acids; organic phosphonates and amino-alkylenepoly(alkylenephosphonates), and
- III) from 0 to 30 % D) of a peroxide from the group consisting of organic mono- or poly-peroxides; organic peracids and salts thereof; persulfates; perborates; percarbonates and persilicates,
- IV) from 0.001 to 1 % E) of a granulate which contains
- a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound of formula (2a), (3), (4), (5), (6) and/or (7) defined above,
- b) from 10 to 60 % by weight of at least one anionic dispersing agent from the group consisting of condensation products of naphthalene-sulfonic acid with formaldehyde; sodium salts of polymerised organic sulfonic acids; (mono-/di-)alkyl-naphthalenesulfonates; polyalkylated polynuclear aryl-sulfonates; sodium salts of polymerised alkylbenzene-sulfonic acids; lignosulfonates; oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl;

and/or at least one water-soluble organic polymer from the group consisting of carboxymethyl cellulose; polyacrylamides; polyvinyl alcohols; polyvinylpyrrolidones; gelatins; hydrolysed polyvinyl acetates; copolymers of vinylpyrrolidone and vinyl acetate; maltodextrins; polyaspartic acid; polyacrylates and polymethacrylates, and

- c) from 15 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof from the group consisting of carbonates; hydrogen carbonates; phosphates; polyphosphates; sulfates; silicates; sulfites; borates; halides; pyrophosphates; aliphatic carboxylic acids having a total number of from 1 to 12 carbon atoms, which are unsubstituted or substituted by hydroxy and/or by amino; aminopolycarboxylates; phytates; phosphonates; aminopolyphosphonates; aminoalkylenepoly(alkylenephosphonates); polyphosphonates; polycarboxylates; water-soluble polysiloxanes; and water-soluble salts used in washing agent and/or washing agent additive formulations, and
- d) from 0 to 10 % by weight of at least one further additive from the group consisting of wetting agents; disintegrants; fillers; water-insoluble or water-soluble dyes or pigments; dissolution accelerators; optical brighteners; aluminium silicates; talc; kaolin; TiO₂; SiO₂; and magnesium trisilicate, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate,
- V) from 0 to 60 % F) of further additives from the group consisting of optical brighteners; suspending agents for dirt; pH regulators; foam regulators; salts for regulating the spray-drying and granulating properties; fragrances; antistatic agents; fabric conditioners; enzymes; bleaching agents; pigments; toning agents; polymers which, during the washing of textiles, prevent staining caused by dyes in the washing liquor which have been released from the textiles under the washing conditions; and perborate activators, and
- VI) from 0 to 5 % G) water.

The granulates E) are prepared, for example, in the following manner:

Firstly, an aqueous solution of the phthalocyanine compound is prepared, to which there is added at least one dispersing agent and/or at least one polymer and at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof and, where appropriate, further additives; stirring is carried out, where appropriate with heating, until a homogeneous solution (or a dilute suspension if water-insoluble additives are used) is obtained. The solids content of the solution obtained should preferably be at least 15 % by weight, especially from 20 to 45 % by weight, based on the total weight of the mixture. The viscosity of the solution is preferably below 600 mPas. The phthalocyanine is preferably present in the slurry in the dissolved state.

The aqueous solution (or suspension) of the phthalocyanine compound is then subjected to a drying step in which all water, with the exception of a residual amount, is removed, solid particles (granules) simultaneously being formed. Known methods are suitable for producing the granulates from the aqueous solution. In principle, both continuous methods and discontinuous methods are suitable. Continuous methods are preferred, especially spray-drying and fluidised bed granulation processes.

Especially suitable are spray-drying processes in which the active ingredient solution is sprayed into a chamber with circulating hot air. The atomisation of the solution is carried out using single or binary nozzles or is brought about by the spinning effect of a rapidly rotating disc. In order to increase the particle size, the spray-drying process may be combined with additional agglomeration of the liquid particles with solid nuclei in a fluidised bed that forms an integral part of the chamber (so-called fluidised spray). The fine particles (< 100 µm) obtained by a conventional spray-drying process may, if necessary after being separated from the exhaust gas flow, be fed as nuclei, without being further treated, directly into the spray cone of the atomiser of the spray-dryer, for the purpose of agglomeration with the liquid droplets of the active ingredient. During the granulation step, the water can be rapidly removed from the solutions comprising phthalocyanine compound, dispersing agent and/or organic polymer, salt and, where appropriate, further additives, and it is expressly intended that agglomeration of the droplets forming in the spray cone, i.e. the agglomeration of droplets with solid particles, will take place. Preference is given to the use of agglomeration processes to produce the granulates according to the invention because such processes usually yield a higher bulk weight so that the granulates have better compatibility with washing agent formulations.

A further embodiment of the present invention comprises using, for preparation of the granulates, phthalocyanine solutions that have been purified by membrane separation procedures.

If necessary, the granules formed in the spray-dryer are removed in a continuous process, for example by a sieving operation. The fines and the oversize particles are either recycled directly to the process (without being redissolved) or are dissolved in the liquid active ingredient formulation and subsequently granulated again.

The residual water content of the granulates E) may be from 3 to 15 % by weight.

The granulates are resistant to abrasion, low in dust, free-flowing and can be readily metered. They are distinguished especially by very rapid solubility in water.

The granulates E) preferably have a density in the range from 500 to 900 g/l, dissolve rapidly in water and do not float on the surface of the washing agent solution. They may be added in the desired concentration of the phthalocyanine compound directly to the washing agent formulation.

The content of granulates E) in accordance with the invention in the formulations according to the invention is from to 0.001 to 1 % by weight, preferably from 0.001 to 0.05 % by weight and very especially from 0.005 to 0.03 % by weight.

The washing agent formulation according to the invention can be prepared in a generally known manner.

A formulation in powder form can be prepared, for example, by first preparing an initial powder by spray-drying an aqueous slurry comprising all of the afore-mentioned components except for components D) and E) and then adding the dry components D) and E) and mixing all of them together. It is also possible to start from an aqueous slurry which, although comprising components A) and C), does not comprise component B) or comprises only a portion of component B). The slurry is spray-dried; component E) is then mixed with component B) and added; and then component D) is mixed in dry. The components are preferably mixed with one another in such amounts that a solid compact washing agent composition in granule form is obtained, having a specific weight of at least 500 g/l.

In another preferred embodiment, the production of the washing agent composition is carried out in three steps. In the first step a mixture of anionic surfactant (and, where appropriate, a small amount of non-ionic surfactant) and builder substance is prepared. In the second step that mixture is sprayed with the major portion of the non-ionic surfactant and then, in the third step, peroxide and, where appropriate, catalyst, and the granulate according to the invention are added. That method is usually carried out in a fluidised bed. In a further preferred embodiment, the individual steps are not carried out completely separately, so that there is a certain amount of overlap between them. Such a method is usually carried out in an extruder, in order to obtain granulates in the form of "megapearls".

As an alternative thereto, the granulates according to the invention can, for the purpose of admixture with a washing agent in a post-dosing step, be mixed with other washing agent components such as phosphates, zeolites, brighteners or enzymes.

A mixture of that kind for post-dosing of the granulates is distinguished by a homogeneous distribution of the granulates according to the invention in the mixture and can consist of, for example, from 5 to 50 % granulates and from 95 to 50 % sodium tripolyphosphate. Where the dark appearance of the granulate in the washing agent composition is to be suppressed, this can be achieved, for example, by embedding the granules in droplets of a whitish meltable substance ("water-soluble wax") or, preferably, by encapsulating the granules in a melt consisting of, for example, a water-soluble wax, as described in EP-B-0 323 407 B1, a white solid (e.g. titanium dioxide) being added to the melt in order to reinforce the masking effect of the capsule.

A further aspect of the present invention relates to novel granulates E) which contain

- a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound, based on the total weight of the granulate,
- b) from 10 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, based on the total weight of the granulate,
- c) from 15 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof, based on the total weight of the granulate,
- d) from 0 to 10 % by weight of at least one further additive, based on the total weight of the granulate, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate,

with the proviso that they do not contain ethoxylated stearylphenyloxyethyldiethyltriamine.

All the preferences mentioned hereinbefore apply to the novel granulates E) according to the invention.

A further aspect of the present invention relates to novel preferred granulates E) which contain

- a) from 4 to 30 % by weight of at least one water-soluble phthalocyanine compound,
- b) from 12 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer,
- c) from 20 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof,
- d) from 0 to 5 % by weight of at least one further additive, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate,

with the proviso that they do not contain ethoxylated stearylphenyloxyethyldiethyltriamine.

A further aspect of the present invention relates to novel, more especially preferred, granulates E) which contain

- a) from 5 to 20 % by weight of at least one water-soluble phthalocyanine compound,
- b) from 12 to 55 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer,
- c) from 25 to 70 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof,
- d) from 0 to 5 % by weight of at least one zeolite compound and, where appropriate, further additives, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate,

with the proviso that they do not contain ethoxylated stearylphenyloxyethyldiethyltriamine.

A further aspect of the present invention relates to novel, likewise more especially preferred, granulates E) which contain

- a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound of formula (2a), (3), (4), (5), (6) and/or (7) defined above, and
- b) from 10 to 60 % by weight of at least one anionic dispersing agent from the group consisting of condensation products of naphthalene-

sulfonic acid with formaldehyde; sodium salts of polymerised organic sulfonic acids; (mono-/di-)alkyl-naphthalenesulfonates; polyalkylated polynuclear aryl-sulfonates; sodium salts of polymerised alkylbenzene-sulfonic acids; lignosulfonates; oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl;

and/or at least one water-soluble organic polymer from the group consisting of carboxymethyl cellulose; polyacrylamides; polyvinyl alcohols; polyvinylpyrrolidones; gelatins; hydrolysed polyvinyl acetates; copolymers of vinylpyrrolidone and vinyl acetate; maltodextrins; polyaspartic acid; polyacrylates and polymethacrylates, and

c) from 15 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof from the group consisting of carbonates; hydrogen carbonates; phosphates; polyphosphates; sulfates; silicates; sulfites; borates; halides; pyrophosphates; aliphatic carboxylic acids having a total number of from 1 to 12 carbon atoms, which are unsubstituted or substituted by hydroxy and/or by amino; aminopolycarboxylates; phytates; phosphonates; aminopolyphosphonates; aminoalkylenepoly(alkylenephosphonates); polyphosphonates; polycarboxylates; water-soluble polysiloxanes; and water-soluble salts used in washing agent and/or washing agent additive formulations, and

d) from 0 to 10 % by weight of at least one further additive from the group consisting of wetting agents; disintegrants; fillers; water-insoluble or water-soluble dyes or pigments; dissolution accelerators; optical brighteners; aluminium silicates; talc; kaolin; TiO₂; SiO₂; and magnesium trisilicate, and

e) from 3 to 15 % by weight water, based on the total weight of the granulate,

with the proviso that they do not contain ethoxylated stearyl diphenyloxyethyl diethyltriamine.

Preferred granulates are as defined hereinbefore, with the proviso that they are not encapsulated and have a substantially homogeneous distribution of ingredients.

All the preferences described hereinbefore for the granulate E) in the washing agent formulation according to the invention apply to constituents a) to e) of the novel granulate according to the invention.

The following Examples serve to illustrate the invention, without limiting the invention thereto. For that purpose, on the one hand, compositions and the preparation of solutions comprising the phthalocyanine compounds are described and, on the other hand, it is described how, using different technologies, those solutions are further processed in order to prepare the granulates according to the invention. Unless otherwise specified, parts and percentages are based on weight. Temperatures are, unless otherwise specified, in degrees Celsius.

Composition of, and preparation of, solutions of phthalocyanine compounds:

Example 1:

564 g of an aqueous solution of an aluminium phthalocyanine compound, which solution has been purified of organic by-products by membrane separation procedures and has a solids content of 19.5 % by weight, are introduced into a glass beaker. To that solution there are added 1857 g of an aqueous solution containing 541 g of an anionic dispersing agent (condensation product of naphthalenesulfonic acid and formaldehyde) and 270 g of sodium sulfate. The aqueous solution is homogenised by stirring at 25°C for 1 hour. A solution having a solids content of 38 % is obtained, the proportions in the dissolved material being 12 % by weight of the phthalocyanine compound, 59 % by weight of the dispersing agent/polymer and 29 % by weight of the salt.

Examples 2 - 11:

The following solutions of phthalocyanine compounds are prepared by the same method. The phthalocyanine solutions used were purified of organic by-products by membrane separation procedures. Where a zeolite or cellulose are used as additives, they can be suspended in the aqueous solution of phthalocyanine compound, dispersing agent/polymer and salt. Table 1 gives the solids content and the percentage proportions of the respective components in the dissolved solids.

Table 1: Examples 2 - 11

Example	2	3	4	5	6	7	8	9	10	11
a) Phthalocyanine compound										
Aluminium phthalocyanine	11		10	5	3	5	8	11		7
Zinc phthalocyanine		12	8	2.4	12	10	8		10	3
b) Dispersing agent/polymer										
Sodium salt of polymerised alkylnaphthalenesulfonic acid			25							
Condensation product of formaldehyde with naphthalenesulfonic acid	13				52			16	39	
Oxylignosulfonate, sodium salt										
Alkylnaphthalenesulfonic acid, sodium salt				31						
Dinaphthylmethanesulfonic acid, sodium salt										
Sodium lignosulfonate			23	31						
Methylene-linked condensation product of arylsulfonic acids and hydroxyarylsulfonic acids		9	2			17	13	12		51
Maltodextrin	14	4				6				
c) Salt/acid										
Sodium sulfate	49	45		30	32	36	71	61	45	39
Sodium carbonate				11						
Sodium citrate			30				18			
Sodium phosphate				12			8			
Polyphosphate, sodium salt	13				1				6	
Sodium chloride				9						
d) Additives										
Fibrous cellulose					0.6					
Solids content of the solutions (% by weight)	28	24	30	33	32	31	23	25	27	33

Example 12:

560 g of an aqueous solution of a zinc phthalocyanine compound, which solution has been purified of organic by-products by membrane separation procedures and has a solids content of 12.5 % by weight, are introduced into a glass beaker and heated to 40°C. A solution of 160 g of a dry pulverulent anionic dispersing agent (condensation product of formaldehyde with naphthalenesulfonic acid) and 50 g of a maltodextrin in 1613 g of water is added to the heated solution. Then 300 g of sodium sulfate, 160 g of sodium citrate and 100 g of sodium tripolyphosphate are added in portions to the solution and finally 200 g of a previously prepared aqueous polyaspartic acid solution (solids content: 20 % by weight) are added. The solution obtained has a solids content of 28 % and is stirred further at 40°C until the solids have completely dissolved. The proportions of the phthalocyanine compound, dispersing agent/polymer and salts are 8 % by weight, 28 % by weight and 64 % by weight, respectively.

Examples 13 to 22:

Solutions having the following compositions are prepared by the same method as in Example 12. The phthalocyanine solutions used were purified of organic by-products by membrane separation procedures. Where a zeolite or cellulose are used as additives, they can be suspended in the aqueous solution of phthalocyanine compound, dispersing agent/polymer and salt. Table 2 below gives the percentage proportions (% by weight) of the respective components in the solids content.

Table 2: Examples 13 - 22

Example	13	14	15	16	17	18	19	20	21	22
a) Phthalocyanine compound										
Aluminium phthalocyanine	11	6	4		13	5	6	4	5	2
Zinc phthalocyanine	10	3	14	15		6		5	4.2	9
b) Dispersing agent/polymer										
Sodium salt of polymerised alkylnaphthalenesulfonic acid							16			
Condensation product of formaldehyde with naphthalenesulfonic acid		50			14		27		50	
Oxylignosulfonate, sodium salt								16		
Alkylnaphthalenesulfonic acid, sodium salt								12		7.4
Sodium lignosulfonate	23									
Dinaphthylmethanesulfonic acid, sodium salt						1		5		
Methylene-linked condensation product of arylsulfonic acids and hydroxyarylsulfonic acids	25			14		10			8.8	30
Maltodextrin				9	10		11			
Polyaspartic acid			12	2		4				
Polyvinyl alcohol								3		
Vinylpyrrolidone/vinyl acetate copolymer							1			
Carboxymethyl cellulose					2					
Polyacrylate	3									
Polyacrylamide								1		
Gelatin							2			
c) Salt/acid										
Sodium sulfate	18	37	70	36	35	74	19	15	29	45
Sodium citrate	6			16	16			20		5.5
Sodium phosphate		4					8			
Polyphosphate, sodium salt	1			8	10			4		
Sodium chloride	3						10	15		
d) Additives										
Zeolite									3	1.1
Solids content of the solutions (% by weight)	35	32	22	24	25	23	30	24	28	26

Examples 23 – 70**Preparation of granulates from the solutions of Examples 1 to 22**

Preparation of the granulates is carried out, as mentioned already, by removing all water, except for the residual moisture, from the solutions prepared above, by means of a drying step. Merely by simply drying the solutions in a vacuum cabinet and comminuting the resulting solid in a mixer, followed by sieving, particles having very good dissolution characteristics can be obtained. Preferred granulation methods consist of drying and simultaneous granulation in a spray-dryer, a disc tower, a bench fluidised spray-dryer or in a fluidised bed granulator. The Examples that follow illustrate the invention, without limiting it thereto.

Example 23:

The solution prepared in Example 1, consisting of phthalocyanine compound, salt and dispersing agent, is spray-dried in a spray-dryer equipped with a single nozzle. The inlet air temperature is 190°C with an exhaust air temperature of 105°C. The product obtained is a free-flowing granulate having an average particle size of 70 µm and a bulk density of 520 g/l with a residual water content of 6 % by weight. The granulate thereby prepared contains 11 % by weight aluminium phthalocyanine compound, 56 % by weight dispersing agent and 27 % by weight salt.

Examples 24 – 33:

Using the same method as in Example 23, granulates are prepared from some of the solutions described in Examples 2 to 22 by spray-drying, the compositions of the granulates being given in Table 3. The granulates are free-flowing with an average particle diameter in the range 50 – 80 µm and have a bulk density of 500 – 550 g/l.

Table 3: Examples 24 – 33

Ex.	Solution from Ex.	a) Phthalocyanine, % by weight	b) Disp./pol., % by weight	c) Salt/acid, % by weight	d) Additive, % by weight	Water, % by weight
24	2	10	25	58	—	7
25	5	7	55	32	1	5
26	6	14	48	30	—	8
27	8	15	12	65	—	8
28	10	10	37	49	—	4
29	11	9	47	36	—	8
30	13	20	48	26	—	6
31	17	12	24	57	—	7
32	19	6	53	34	—	7
33	21	9	55	27	3	6

Example 34:

Preparation of the granulates is carried out by spray-drying the solutions described in Examples 1 to 22. In contrast to the method of Examples 23 to 33, the fines produced during the drying process are continuously separated off from the exhaust air stream and passed directly into the spray cone of the nozzle tower by means of a gas stream. The granulates thereby produced are much coarser and also denser than those of Examples 22 to 33 and have a much reduced fines content (less than 5 % of particles below 20 µm). The average particle size is 110 µm with a bulk density of 540 – 580 g/l.

Example 35:

The solution prepared in Example 3, consisting of phthalocyanine compound, polymer, salt and dispersing agent, is spray-dried in a drying tower equipped with a disc atomiser. The inlet air temperature is 205°C with an exhaust air temperature of 102°C. The product obtained is a free-flowing granulate having an average particle size of 65 µm and a bulk density of 510 g/l with a residual water content of 7 % by weight. The granulate thereby prepared contains 12 % by weight dispersing agent/polymer, 70 % by weight salt and 11 % by weight zinc phthalocyanine compound.

Examples 36 - 43:

Using the same method as in Example 35, granulates are prepared from some of the solutions described in Examples 1 to 22 by spray-drying in a disc tower. The granulates are free-flowing with an average particle diameter of 70 µm and have a bulk density of 520 – 540 g/l. Their compositions are given in Table 4.

Table 4: Examples 36 – 43

Ex.	Solution from Ex.	a) Phthalocyanine, % by weight	b) Disp./pol., % by weight	c) Salt/acid, % by weight	d) Additive, % by weight	Water, % by weight
36	5	7	53	31	1	8
37	7	14	22	58	–	6
38	8	15	13	68	–	4
39	9	10	26	57	–	7
40	14	8	46	38	–	8
41	15	17	12	67	–	4
42	17	12	25	58	–	5
43	22	10	35	48	1	6

Example 44:

The solution prepared in Example 11 is granulated in a bench fluidised spray-dryer. In the first phase of the granulation process, nuclei are built up in the fluidised bed (inlet air temperature 200°C, bed temperature 95°C). Once sufficient nuclei have been built up in the bed, the bed temperature is lowered to about 48°C in order to initiate granulation. Granulation of the entire solution is carried out in a range for the bed temperature of from 47 to 50°C. The granulate obtained has a residual moisture content of 9 % at the outlet from the granulator and is subsequently dried in a continuously operating fluid bed with warm air to a desired value of 6 %. The product obtained is a free-flowing granulate having an average particle size of 130 µm and a bulk density of 610 g/l, with proportions of 9 % by weight phthalocyanine compound, 48 % by weight dispersing agent/polymer and 37 % by weight salt in the solid material.

Examples 45 – 57:

Using the same method as in Example 44, granulates are prepared from solutions of Examples 1 to 22 by granulating in a bench fluidised spray-dryer and, where appropriate,

subsequently drying in a continuously operated fluid bed. The granulates obtained are free-flowing with an average particle diameter of around 120 – 150 µm and, depending on the composition of the active-ingredient-containing solution and the granulation parameters, have a bulk density of 500 – 800 g/l. The compositions of the granulates are listed in Table 5.

Table 5: Examples 45 – 57

Ex.	Solution from Ex.	a) Phthalocyanine, % by weight	b) Disp./pol., % by weight	c) Salt/acid, % by weight	d) Additive, % by weight	Water, % by weight
45	1	11	54	27	–	8
46	2	10	24	55	–	11
47	4	17	48	30	–	5
48	5	7	53	31	1	8
49	6	14	49	31	–	6
50	9	10.5	27	58	–	4.5
51	12	7	26	60	–	7
52	13	19	47	26	–	8
53	14	8	46	38	–	8
54	16	14	23	55	–	8
55	18	11	14	70	–	5
56	20	9	35	51	–	5
57	21	9	55	27	3	6

Example 58:

A portion of the solution prepared in Example 22, consisting of phthalocyanine compound, salt, dispersing agent and zeolite, is dried *in vacuo* for 24 hours and the solid obtained is comminuted in a laboratory mixer. The product obtained is transferred to a laboratory fluidised bed granulator (STREA-1, Aeromatic AG, Bubendorf, Switzerland) as granulating nuclei and fluidised by means of warm air (about 65°C) flowing in through the perforated tray. The solution of Example 6 is continuously sprayed into that fluidised bed using a binary nozzle. After about 120 minutes and after the introduction of about 4000 g of solution, granulation is terminated by stopping the introduction of solution. The granulates obtained are dried in the same apparatus, using warm air at 80°C, to a residual moisture content of 8 % by weight. After discharging the product, the fines are removed from the granulate by

sieving. A free-flowing granulate is obtained having an average particle size of 310 µm and a bulk density of 680 g/l. The proportions in the solid material are 10 % by weight for the phthalocyanine compounds, 34 % by weight for the dispersing agents, 47 % by weight for the salts and 1 % by weight for the zeolite.

Examples 59 – 70:

Using the same method as in Example 58, granulates are prepared from solutions of Examples 1 to 21. These granulates are free-flowing with an average particle diameter of around 220 – 350 µm and have a bulk density of 600 – 750 g/l. The compositions of the granulates are given in Table 6.

Table 6: Examples 59 – 70

Ex.	Solution from Ex.	a) Phthalocyanine, % by weight	b) Disp./pol., % by weight	c) Salt/acid, % by weight	d) Additive, % by weight	Water, % by weight
59	1	11	55	27	–	7
60	3	11	12	68	–	9
61	4	17	47	30	–	6
62	5	7	53	31	1	8
63	6	14	48	31	–	7
64	9	10	26	56	–	8
65	10	9	35	45	–	11
66	12	7	25	56	–	12
67	13	20	48	26	–	6
68	14	9	48	39	–	4
69	19	6	52	34	–	8
70	21	9	55	27	3	6

Washing agent preparations comprising the granulates according to the invention

Examples 71 to 88 illustrate the use of the granulates according to the invention in washing agent preparations, without limiting it thereto.

Table 7: Examples 71 - 80

Examples	71	72	73	74	75	76	77	78	79	80
Constituents (% by weight)										
A)										
Sodium salt of lauryl benzenesulfonic acid	10	10	10	10	10	10	10	10	10	10
Sodium lauryl ether sulfate (AES)	3	3	3	3	3	3	3	3	3	3
B)										
Neodol 23-6.5E (alcohol ethoxylate)	4	4	4	4	4	4	4	4	4	4
C)										
Zeolite A (sodium aluminium silicate)	25	20	22	35	10	25		32	25	
Sodium tripolyphosphate		10			30		35		5	32
D)										
Sodium percarbonate	20	20	20	5		20				
Sodium perborate							20		20	20
NOBS (p-nonenoyl-oxybenzenesulfonate)						3	3		3	
E)										
Granulates, Ex. 23-70	0.03	0.01	0.01	0.02	0.02	0.005	0.02	0.005	0.01	0.02
F)										
Perfume	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cellulase	1.5		1.5	1.5	1.5					
Protease		1.5				1.5	1.5	1.5	1.5	1.5
Polycarboxylate		4				4	4	4	4	4
Carboxymethyl cellulose	2	2	2	2	2	2	2	2	2	2
Sodium sulfate	15	13	18	25	22	20	9	25	8	10
Sodium carbonate	10	7	10	7	7		5	13	8	6
TAED (tetraacetyl-ethylenediamine)	3	3	3	1						3

Further additives in small amounts (foam inhibitors etc.) and the residual moisture content of the washing agent formulation make the composition up to 100 %.

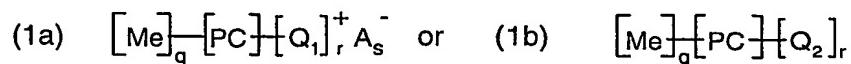
Table 8: Examples 81 – 88

Examples	81	82	83	84	85	86	87	88
Sodium salt of lauryl benzenesulfonic acid	8%	8%	8%	8%	8%	8%	8%	8%
Sodium lauryl ether sulfate (AES)	3%	3%	3%	3%	3%	3%	3%	3%
Neodol 23-6.5E (non-ionic alcohol ethoxylate)	5%	5%	5%	5%	5%	5%	5%	5%
Zeolite A	20%	20%	20%	20%	20%	20%	20%	20%
Polycarboxylate (co-builder)	5%	5%	5%	5%	5%	5%	5%	5%
Sodium carbonate	18%	18%	18%	18%	18%	18%	18%	18%
Sodium silicate	4%	4%	4%	4%	4%	4%	4%	4%
Sodium sulfate	5%	5%	5%	5%	5%	5%	5%	5%
Hydroxyethanediphosphonic acid (complexer)	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%
Cellulase	1.5%	1.5%		1.5%	1.5%		1.5%	1.5%
Protease			1.5%			1.5%		
Carboxymethyl cellulose	1%	1%	1%	1%	1%	1%	1%	1%
Sodium perborate monohydrate	15%	15%	15%	15%	15%	15%	15%	15%
TAED	5%	5%	5%	5%	5%	5%	5%	5%
Soap	2%	2%	2%	2%	2%	2%	2%	2%
Granulate E)	0.03	0.005	0.02	0.008	0.01	0.03	0.02	0.02

Further additives in small amounts and the residual moisture content of the washing agent formulation make the composition up to 100 %.

What is claimed is:

1. A formulation comprising at least one granulate containing
 - a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound, based on the total weight of the granulate,
 - b) from 10 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, based on the total weight of the granulate,
 - c) from 15 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof, based on the total weight of the granulate,
 - d) from 0 to 10 % by weight of at least one further additive, based on the total weight of the granulate, and
 - e) from 3 to 15 % by weight water, based on the total weight of the granulate.
2. A formulation according to claim 1, wherein the granulate comprises, as phthalocyanine compound, at least one water-soluble Zn(II), Fe(II), Ca(II), Mg(II), Na(I), K(I), Al, Si(IV), P(V), Ti(IV), Ge(IV), Cr(VI), Ga(III), Zr(IV), In(III), Sn(IV) or Hf(VI) phthalocyanine compound.
3. A formulation according to either claim 1 or claim 2, wherein the granulate comprises at least one phthalocyanine compound of formula



wherein

PC is the phthalocyanine ring system;

Me is Zn; Fe(II); Ca; Mg; Na; K; Al-Z₁; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV); In(III); Sn(IV) or Hf(VI);

Z₁ is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion;

q is 0, 1 or 2;

r is from 1 to 4;

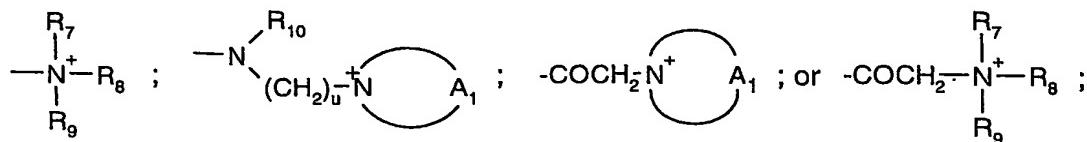
Q₁ is a sulfo or carboxy group; or is a radical of formula
 $-\text{SO}_2\text{X}_2\text{-R}_6\text{-X}_3^+$; $-\text{O-R}_6\text{-X}_3^+$; or $-(\text{CH}_2)_t\text{-Y}_1^+$;

wherein

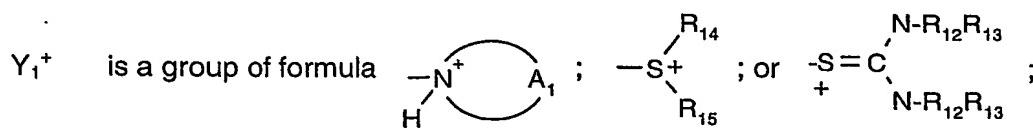
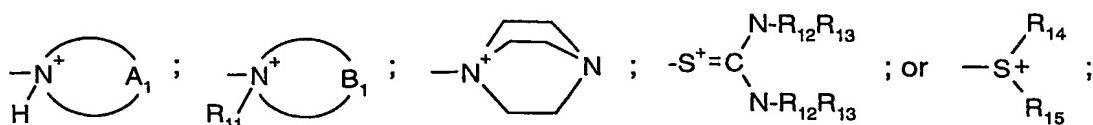
R_6 is branched or unbranched C_1 - C_8 alkylene; or 1,3- or 1,4-phenylene;

X_2 is -NH-; or -N-C₁-C₅alkyl-;

X_3^+ is a group of formula



and, in the case where R_6 = C_1 - C_8 alkylene, may also be a group of formula



t is 0 or 1;

in which above formulae,

R_7 and R_8 are each independently of the other C_1 - C_6 alkyl;

R_9 is C_1 - C_6 alkyl; C_5 - C_7 cycloalkyl; or $NR_{11}R_{12}$;

R_{10} and R_{11} are each independently of the other C_1 - C_5 alkyl;

R_{12} and R_{13} are each independently of the other hydrogen or C_1 - C_5 alkyl;

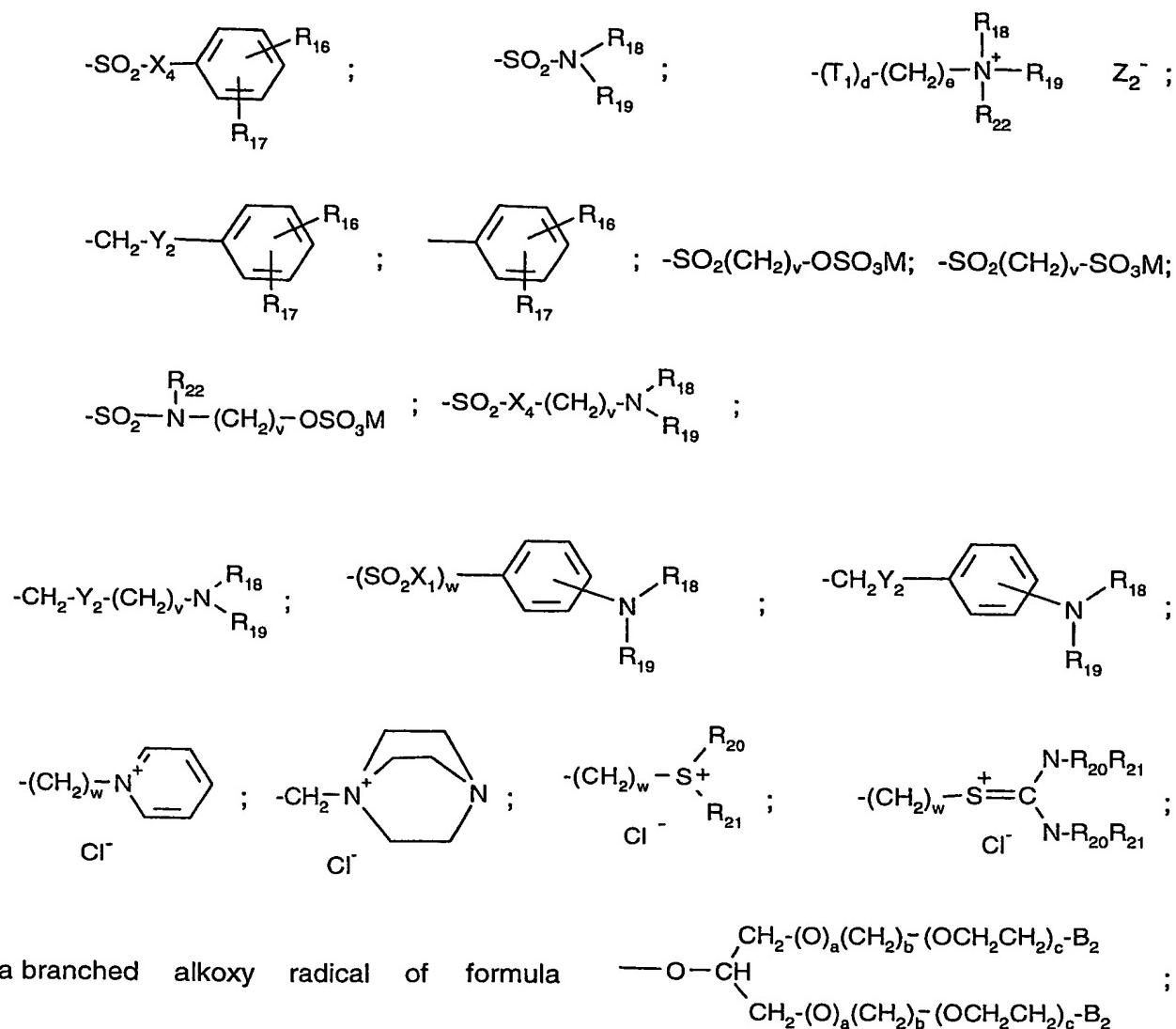
R_{14} and R_{15} are each independently of the other unsubstituted or hydroxy-, cyano-, carboxy-, C_1 - C_6 alkoxy-carbonyl-, C_1 - C_6 alkoxy-, phenyl-, naphthyl- or pyridyl-substituted C_1 - C_6 alkyl;

u is from 1 to 6;

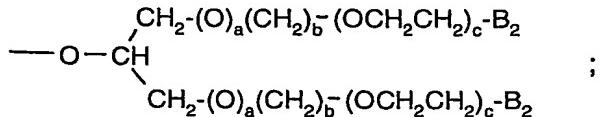
A_1 is the balance of an aromatic 5- to 7-membered nitrogen heterocycle which may contain one or two further nitrogen atoms as ring members, and

B_1 is the balance of a saturated 5- to 7-membered nitrogen heterocycle which may contain 1 or 2 further nitrogen, oxygen and/or sulfur atoms as ring members;

Q_2 is hydroxy; C_1 - C_{22} alkyl; branched C_3 - C_{22} alkyl; C_2 - C_{22} alkenyl; branched C_4 - C_{22} alkenyl or a mixture thereof; C_1 - C_{22} alkoxy; a sulfo or carboxy radical; a radical of formula



a branched alkoxy radical of formula



--O--CH_2
 $\text{CH}(\text{O})_a(\text{CH}_2)_b\text{--}(\text{OCH}_2\text{CH}_2)_c\text{--B}_2$; an alkylethyleneoxy unit of formula
 $\text{CH}_2(\text{O})_a(\text{CH}_2)_b\text{--}(\text{OCH}_2\text{CH}_2)_c\text{--B}_2$

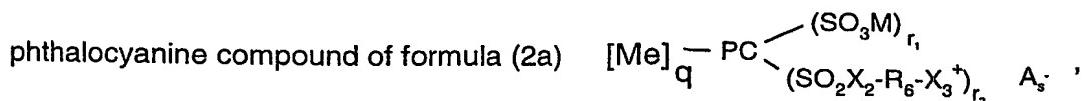
$-(T_1)_d-(CH_2)_b(OCH_2CH_2)_a-B_3$ or an ester of formula COOR₂₃,

wherein

B₂ is hydrogen; hydroxy; C₁-C₃₀alkyl; C₁-C₃₀alkoxy; -CO₂H; -CH₂COOH; SO₃⁻M₁; -OSO₃⁻M₁; -PO₃²⁻M₁; -PPO₃²⁻M₁; or a mixture thereof;
B₃ is hydrogen; hydroxy; -COOH; -SO₃⁻M₁; -OSO₃⁻M₁; or C₁-C₆alkoxy;
M₁ is a water-soluble cation;
T₁ is -O-; or -NH-;

X₁ and X₄ are each independently of the other -O-; -NH-; or -N-C₁-C₅alkyl;
R₁₆ and R₁₇ are each independently of the other hydrogen; a sulfo group or a salt thereof; a carboxy group or a salt thereof, or a hydroxy group, at least one of the radicals R₁₆ and R₁₇ being a sulfo or carboxy group or a salt thereof,
Y₂ is -O-; -S-; -NH- or -N-C₁-C₅alkyl;
R₁₈ and R₁₉ are each independently of the other hydrogen; C₁-C₆alkyl; hydroxy-C₁-C₆alkyl; cyano-C₁-C₆alkyl; sulfo-C₁-C₆alkyl; carboxy- or halo-C₁-C₆alkyl; unsubstituted or halo-, C₁-C₄alkyl-, C₁-C₄alkoxy-, sulfo- or carboxy-substituted phenyl; or R₁₈ and R₁₉, together with the nitrogen atom to which they are bonded, are a saturated 5- or 6-membered heterocyclic ring which may additionally contain a further nitrogen or oxygen atom as ring member;
R₂₀ and R₂₁ are each independently of the other a C₁-C₆alkyl or aryl-C₁-C₆alkyl radical;
R₂₂ is hydrogen; or unsubstituted or halo-, hydroxy-, cyano-, phenyl-, carboxy-, C₁-C₆-alkoxy-carbonyl- or C₁-C₆alkoxy-substituted C₁-C₆alkyl;
R₂₃ is C₁-C₂₂alkyl; branched C₄-C₂₂alkyl; C₁-C₂₂alkenyl or branched C₄-C₂₂alkenyl; C₃-C₂₂-glycol; C₁-C₂₂alkoxy; branched C₄-C₂₂alkoxy; or a mixture thereof;
M is hydrogen; or an alkali metal ion or ammonium ion,
Z₂⁻ is a chlorine ion, bromine ion, alkylsulfate ion or aralkylsulfate ion;
a is 0 or 1;
b is from 0 to 6;
c is from 0 to 100;
d is 0 or 1;
e is from 0 to 22;
v is an integer from 2 to 12;
w is 0 or 1; and
A⁻ is an organic or inorganic anion,
and
s in the case of monovalent anions A⁻ is equal to r and in the case of polyvalent anions is ≤ r, it being necessary for A_s⁻ to balance the positive charge; and when r ≠ 1, the radicals Q₁ may be identical or different,
and wherein the phthalocyanine ring system may also contain further solubility-imparting groups.

4. A formulation according to claim 3, wherein the granulate comprises at least one



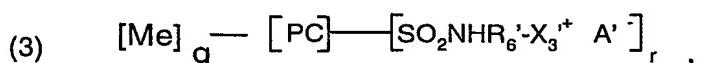
wherein

Me , q , PC , X_2 , X_3 and R_6 are as defined for formula (1a),

M is hydrogen; or an alkali metal ion, ammonium ion or amine salt ion;

and the sum of the numbers r_1 and r_2 is from 1 to 4, and

A_s^- exactly balances the positive charge of the remainder of the molecule, or of formula

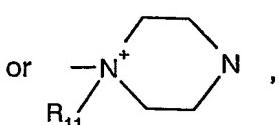
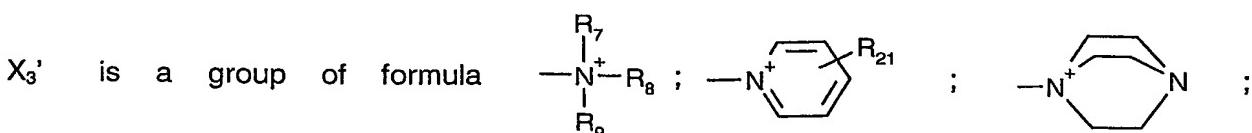


wherein

Me , q and PC are as defined for formula (1a),

R_6' is $\text{C}_2\text{-C}_6$ alkylene;

r is a number from 1 to 4;



wherein

R_7 and R_8 are each independently of the other unsubstituted or hydroxy-, cyano-, halo- or phenyl-substituted $\text{C}_1\text{-C}_4$ alkyl;

R_9 is R_7 ; cyclohexyl or amino;

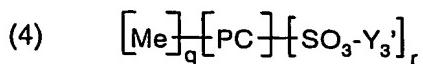
R_{11} is $\text{C}_1\text{-C}_4$ alkyl;

R_{21} is $\text{C}_1\text{-C}_4$ alkyl; $\text{C}_1\text{-C}_4$ alkoxy; halogen; carboxy; $\text{C}_1\text{-C}_4$ alkoxy-carbonyl or hydroxy; and

A'^- is a halide ion, alkylsulfate ion or arylsulfate ion;

it being possible for the radicals $\text{-SO}_2\text{NHR}_6^+\text{-X}_3^+\text{A}'^-$ to be identical or different.

5. A formulation according to claim 3, wherein the granulate comprises at least one phthalocyanine compound of formula



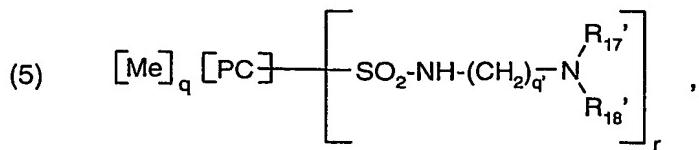
wherein

- PC is the phthalocyanine ring system;
 Me is Zn; Fe(II); Ca; Mg; Na; K; Al-Z₁; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV); In(III); Sn(IV) or Hf(VI);
 Z₁ is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion;
 q is 0; 1; or 2;
 Y₃' is hydrogen; or an alkali metal ion or ammonium ion; and
 r is any number from 1 to 4.

6. A formulation according to claim 5, wherein the granulate comprises at least one phthalocyanine compound of formula (4) wherein

- Me is Zn or Al-Z₁; and
 Z₁ is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion.

7. A formulation according to claim 3, wherein the granulate comprises at least one phthalocyanine compound of formula

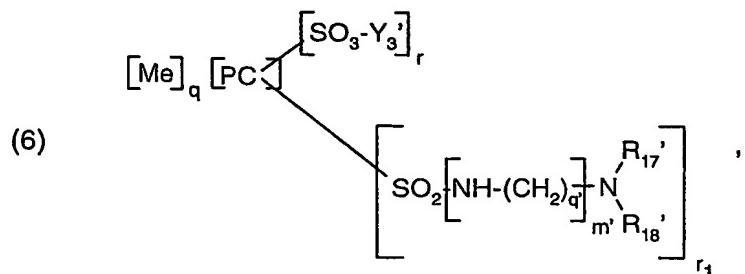


wherein

- PC, Me and q are as defined for formula (4);
 R₁₇' and R₁₈' are each independently of the other hydrogen; phenyl; sulfophenyl; carboxyphenyl; C₁-C₆alkyl; hydroxy-C₁-C₆alkyl; cyano-C₁-C₆alkyl; sulfo-C₁-C₆alkyl; carboxy-C₁-C₆alkyl or halo-C₁-C₆alkyl or, together with the nitrogen atom, form a morpholine ring;
 q' is an integer from 2 to 6; and
 r is a number from 1 to 4;

it being possible, when r > 1, for the radicals $-SO_2-NH-(CH_2)_q-N(R_{17}')_r$ present in the molecule to be identical or different.

8. A formulation according to claim 3, wherein the granulate comprises at least one phthalocyanine compound of formula



wherein

PC, Me and q are as defined for formula (4).

Y_3^- is hydrogen; or an alkali metal ion or ammonium ion.

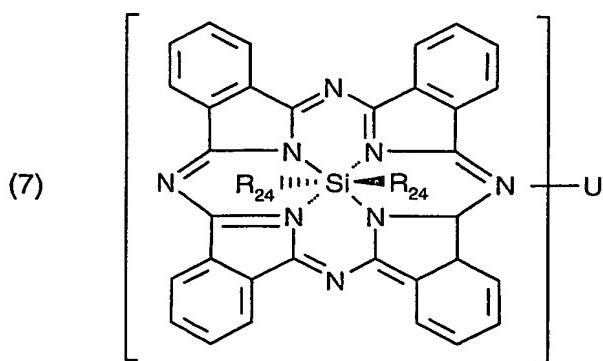
q' is an integer from 2 to 6;

R_{17}' and R_{18}' are each independently of the other hydrogen; phenyl; sulfophenyl; carboxyphenyl; C_1 - C_6 alkyl; hydroxy- C_1 - C_6 alkyl; cyano- C_1 - C_6 alkyl; sulfo- C_1 - C_6 alkyl; carboxy- C_1 - C_6 alkyl or halo- C_1 - C_6 alkyl or, together with the nitrogen atom, form a morpholine ring.

m' is 0 or 1; and

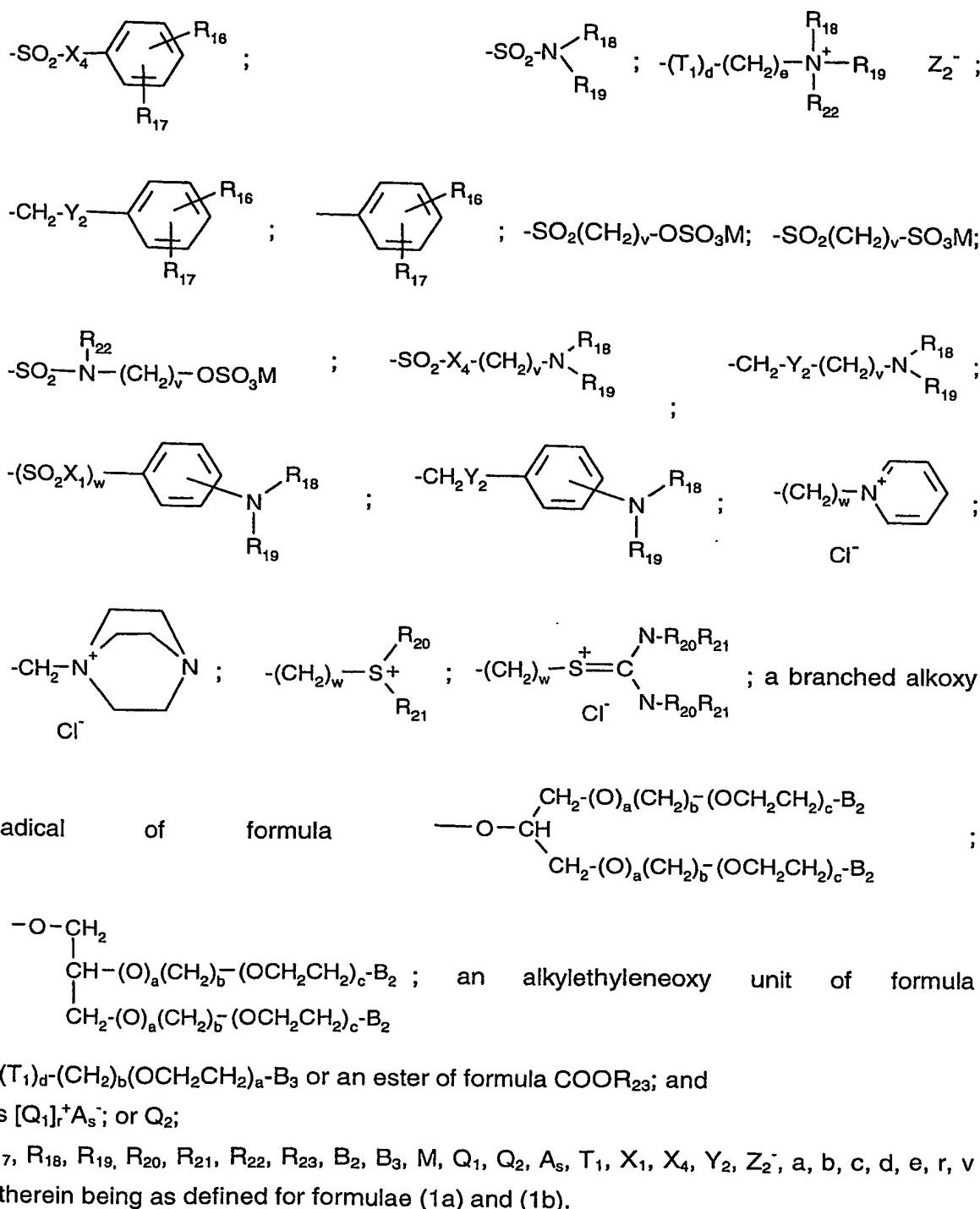
r and r_1 are each independently of the other any number from 0.5 to 3.5, the sum $r + r_1$ being a minimum of 1 and a maximum of 4.

9. A formulation according to claim 3, wherein the granulate comprises at least one phthalocyanine compound of formula



wherein

R_{24} is hydroxy; C₁-C₂₂alkyl; branched C₄-C₂₂alkyl; C₁-C₂₂alkenyl; branched C₄-C₂₂alkenyl or a mixture thereof; C₁-C₂₂alkoxy; a sulfo or carboxy radical; a radical of formula



10. A formulation according to any one of claims 1 to 9, wherein the granulate contains from 4 to 30 % by weight of at least one phthalocyanine compound.

11. A formulation according to any one of claims 1 to 9, wherein the granulate contains from 5 to 20 % by weight of at least one phthalocyanine compound.
12. A formulation according to any one of claims 1 to 11, wherein the granulate contains from 12 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer.
13. A formulation according to any one of claims 1 to 11, wherein the granulate contains from 12 to 55 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer.
14. A formulation according to any one of claims 1 to 13, wherein the granulate comprises, as anionic dispersing agent, one or more condensation products from the following group: condensation products of aromatic sulfonic acids and formaldehyde, condensation products of aromatic sulfonic acids with unsubstituted or chlorinated biphenyls or biphenyl oxides and optionally formaldehyde, (mono-/di-)alkylnaphthalenesulfonates, sodium salts of polymerised organic sulfonic acids, sodium salts of polymerised alkynaphthalenesulfonic acids, sodium salts of polymerised alkylbenzenesulfonic acids, alkylarylsulfonates, sodium salts of alkyl polyglycol ether sulfates, polyalkylated polynuclear arylsulfonates, methylene-linked condensation products of arylsulfonic acids and hydroxyarylsulfonic acids, sodium salts of dialkylsulfosuccinic acids, sodium salts of alkyl diglycol ether sulfates, sodium salts of polynaphthalenemethanesulfonates, ligno- or oxyligno-sulfonates and heterocyclic polysulfonic acids.
15. A formulation according to any one of claims 1 to 13, wherein the granulate comprises, as anionic dispersing agent, a condensation product from the following group: condensation products of naphthalenesulfonic acids with formaldehyde, sodium salts of polymerised organic sulfonic acids, (mono-/di-)alkylnaphthalenesulfonates, polyalkylated polynuclear arylsulfonates, sodium salts of polymerised alkylbenzenesulfonic acid, lignosulfonates, oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl.
16. A formulation according to any one of claims 1 to 15, wherein the granulate comprises, as water-soluble (but not necessarily film-forming) polymer, one or more compounds from the following group:

gelatins, polyacrylates, polymethacrylates, copolymers of ethyl acrylate, methyl methacrylate and methacrylic acid (ammonium salt), polyvinylpyrrolidones, vinylpyrrolidones, vinyl acetates, copolymers of vinylpyrrolidone with long-chain olefins, poly(vinylpyrrolidone/dimethylaminoethyl methacrylates), copolymers of vinylpyrrolidone/dimethylaminopropyl methacrylamides, copolymers of vinylpyrrolidone/dimethylaminopropyl acrylamides, quaternised copolymers of vinylpyrrolidones and dimethylaminoethyl methacrylates, terpolymers of vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of vinylpyrrolidone and methacrylamidopropyltrimethylammonium chloride, terpolymers of caprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of styrene and acrylic acid, polycarboxylic acids, polyacrylamides, carboxymethyl cellulose, hydroxymethyl cellulose, polyvinyl alcohols, hydrolysed and non-hydrolysed polyvinyl acetate, copolymers of maleic acid with unsaturated hydrocarbons and also mixed polymerisation products of the mentioned polymers, polyethylene glycol (MW = 4000 – 20 000), copolymers of ethylene oxide with propylene oxide (MW > 3500), condensation products (block polymerisation products) of alkylene oxide, especially propylene oxide, copolymers of vinylpyrrolidone with vinyl acetate, ethylene oxide-propylene oxide addition products with diamines, especially ethylenediamine, polystyrenesulfonic acid, polyethylene-sulfonic acid, copolymers of acrylic acid with sulfonated styrenes, gum arabic, hydroxypropyl methylcellulose, sodium carboxymethyl cellulose, hydroxypropyl methylcellulose phthalate, maltodextrin, starch, sucrose, lactose, enzymatically modified and subsequently hydrated sugars, as are obtainable under the name "Isomalt", cane sugar, polyaspartic acid and tragacanth.

17. A formulation according to any one of claims 1 to 15, wherein the granulate comprises, as water-soluble polymer, a compound from the following group: carboxymethyl cellulose, polyacrylamides, polyvinyl alcohols, polyvinylpyrrolidones, gelatins, hydrolysed polyvinyl acetates, copolymers of vinylpyrrolidone and vinyl acetate, maltodextrins, polyaspartic acid and also polyacrylates and polymethacrylates.

18. A formulation according to any one of claims 1 to 17, wherein the granulate contains from 20 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid and/or a salt thereof.

19. A formulation according to any one of claims 1 to 17, wherein the granulate contains from 25 to 70 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid and/or a salt thereof.

20. A formulation according to claim 19, wherein the granulate comprises, as inorganic salt and/or low-molecular-weight organic acid and/or a salt thereof, at least one compound from the group consisting of carbonate; hydrogen carbonate; phosphate; polyphosphate; sulfate; silicate; sulfite; borate; halide; pyrophosphate; aliphatic carboxylic acid having a total number of from 1 to 12 carbon atoms, which are unsubstituted or substituted by hydroxy and/or by amino; aminopolycarboxylate; phytate; phosphonate; aminopolyphosphonate; amino-alkylenepoly(alkyleneephosphonate); polyphosphonate; polycarboxylate; water-soluble polysiloxane; and a water-soluble salt used in washing agent and/or washing agent additive formulations.

21. A formulation according to claim 20, wherein the granulate comprises, as low-molecular-weight organic acid, an aliphatic C₂-C₁₂polycarboxylic acid or a salt thereof.

22. A formulation according to claim 21, wherein the granulate comprises, as low-molecular-weight organic acid, oxalic acid, tartaric acid, acetic acid, propionic acid, succinic acid, maleic acid, citric acid, formic acid, gluconic acid, p-toluenesulfonic acid, terephthalic acid, benzoic acid, phthalic acid, acrylic acid and/or polyacrylic acid and/or a salt thereof.

23. A formulation according to any one of claims 1 to 22, wherein the granulate contains from 0 to 5 % by weight of at least one further additive.

24. A formulation according to claim 23, wherein the granulate comprises a wetting agent, a disintegrant, a filler, a water-insoluble or water-soluble dye or pigment, and/or a dissolution accelerator, an optical brightener, a zeolite, talc, powdered cellulose, fibrous cellulose, microcrystalline cellulose, kaolin, TiO₂, SiO₂ and/or magnesium trisilicate.

25. A formulation according to any one of claims 1 to 24, wherein the granulate consists of
a) from 4 to 30 % by weight of at least one water-soluble phthalocyanine compound as defined in any one of claims 2 to 9,

- b) from 12 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, as defined in either claim 14 or claim 15,
- c) from 20 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof, as defined in any one of claims 20 to 22,
- d) from 0 to 5 % by weight at least one further additive as defined in claim 24, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate.

26. A formulation according to any one of claims 1 to 24, wherein the granulate consists of

- a) from 5 to 20 % by weight of at least one water-soluble phthalocyanine compound as defined in any one of claims 2 to 9,
- b) from 12 to 55 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, as defined in either claim 14 or claim 15,
- c) from 25 to 70 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof, as defined in any one of claims 20 to 22,
- d) from 0 to 5 % by weight at least one further additive as defined in claim 24, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate.

27. A formulation according to any one of claims 1 to 24, wherein the granulate consists of

- a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound of formula (2a), (3), (4), (5), (6) and/or (7) defined above,
- b) from 10 to 60 % by weight of at least one anionic dispersing agent from the group consisting of condensation products of naphthalene-sulfonic acid with formaldehyde; sodium salts of polymerised organic sulfonic acids; (mono-/di-)alkyl-naphthalenesulfonates; polyalkylated polynuclear aryl-sulfonates; sodium salts of polymerised alkylbenzene-sulfonic acids; lignosulfonates; oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl; and/or at least one water-soluble organic polymer from the group consisting of carboxymethyl cellulose;

polyacrylamides; polyvinyl alcohols; polyvinylpyrrolidones; gelatins; hydrolysed polyvinyl acetates; copolymers of vinylpyrrolidone and vinyl acetate; maltodextrins; polyaspartic acid; polyacrylates and polymethacrylates, and

- c) from 15 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof from the group consisting of carbonates; hydrogen carbonates; phosphates; polyphosphates; sulfates; silicates; sulfites; borates; halides; pyrophosphates; aliphatic carboxylic acids having a total number of from 1 to 12 carbon atoms, which are unsubstituted or substituted by hydroxy and/or by amino; aminopolycarboxylates; phytates; phosphonates; aminopolyphosphonates; aminoalkylenepoly(alkyleneephosphonates); polyphosphonates; polycarboxylates; water-soluble polysiloxanes; and water-soluble salts used in washing agent and/or washing agent additive formulations, and
- d) from 0 to 10 % by weight of at least one further additive from the group consisting of wetting agents; disintegrants; fillers; water-insoluble or water-soluble dyes or pigments; dissolution accelerators; optical brighteners; aluminium silicates; talc; kaolin; TiO₂, SiO₂; and magnesium trisilicate, and
- e) from 3 to 15 % by weight water, based on the total weight of the granulate.

28. A formulation according to any one of claims 1 to 27, wherein the granulate has an average particle size of < 500 µm.

29. A formulation according to any one of claims 1 to 27, wherein the granulate has an average particle size of from 40 to 400 µm.

30. Use of a formulation according to any one of claims 1 to 29 as a washing agent composition, washing agent additive or additive concentrate.

31. Use of a formulation, according to claim 30, as or in a pre- and/or after-treatment agent, stain-removing salt, washing-power enhancer, fabric conditioner, bleaching agent and/or UV-protection enhancer.

32. Use of a formulation, according to claim 30, in the form of a powder, (super-)compact powder, single- or multi-layer tablet (tab), bar, block, sheet, paste, washing agent gel, or in the form of a powder, paste, gel or liquid packed in capsules or in pouches (sachets).

33. A washing agent formulation according to any one of claims 1 to 29 consisting of

- I) from 5 to 70 % A) of at least one anionic surfactant and/or B) at least one non-ionic surfactant, based on the total weight of the washing agent formulation,
- II) from 5 to 60 % C) of at least one builder substance, based on the total weight of the washing agent formulation,
- III) from 0 to 30 % D) of at least one peroxide and, optionally, at least one activator, based on the total weight of the washing agent formulation, and
- IV) from 0.001 to 1 % E) of at least one granulate as defined in any one of claims 1 to 29, and
- V) from 0 to 60 % F) of at least one further additive, and
- VI) from 0 to 5 % G) water.

34. A washing agent formulation according to claim 33, consisting of

- I) from 5 to 70 % A) of at least one anionic surfactant from the group consisting of alkylbenzenesulfonates having from 9 to 15 carbon atoms in the alkyl radical; alkyl-naphthalenesulfonates having from 6 to 16 carbon atoms in the alkyl radical; and alkali metal sarcosinates of the formula R-CO-N(R₁)-CH₂COOM₁,
wherein R is alkyl or alkenyl having from 8 to 18 carbon atoms in the alkyl or alkenyl radical,
R₁ is C₁-C₄alkyl and
M₁ is an alkali metal and/or
- B) at least one non-ionic surfactant from the group consisting of condensation products of from 3 to 8 mols

- of ethylene oxide with 1 mol of primary alcohol containing from 9 to 15 carbon atoms,
- II) from 5 to 60 % C) of a builder substance from the group consisting of alkali metal phosphates; carbonates; hydrogen carbonates; silicates; aluminium silicates; polycarboxylates; polycarboxylic acids; organic phosphonates and aminoalkylenepoly(alkylenephosphonates), and
- III) from 0 to 30 % D) of a peroxide from the group consisting of organic mono- or poly-peroxides; organic peracids and salts thereof; persulfates; perborates; percarbonates and persilicates,
- IV) from 0.001 to 1 % E) of a granulate which contains
- a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound of formula (2a), (3), (4), (5), (6) and/or (7) defined above, and
 - b) from 10 to 60 % by weight of at least one anionic dispersing agent from the group consisting of condensation products of naphthalene-sulfonic acid with formaldehyde; sodium salts of polymerised organic sulfonic acids; (mono-/di-)alkyl-naphthalenesulfonates; polyalkylated polynuclear aryl-sulfonates; sodium salts of polymerised alkylbenzenesulfonic acids; lignosulfonates; oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl; and/or at least one water-soluble organic polymer from the group consisting of carboxymethyl cellulose; polyacrylamides; polyvinyl alcohols; polyvinylpyrrolidones; gelatins; hydrolysed polyvinyl acetates; copolymers of vinylpyrrolidone and vinyl acetate; maltodextrins; polyaspartic acid; polyacrylates and polymethacrylates, and
 - c) from 15 to 75 % by weight of at least one inorganic salt and/or a least one low-molecular-weight organic acid or a salt thereof from the group consisting of carbonates; hydrogen carbonates; phosphates; polyphosphates; sulfates; silicates; sulfites;

borates; halides; pyrophosphates; aliphatic carboxylic acids having a total number of from 1 to 12 carbon atoms, which are unsubstituted or substituted by hydroxy and/or by amino; aminopolycarboxylates; phytates; phosphonates; aminopolyphosphonates; aminoalkylenephosphonates; polyphosphonates; polycarboxylates; water-soluble polysiloxanes; and water-soluble salts used in washing agent and/or washing agent additive formulations, and

d) from 0 to 10 % by weight of at least one further additive from the group consisting of wetting agents; disintegrants; fillers; water-insoluble or water-soluble dyes or pigments; dissolution accelerators; optical brighteners; aluminium silicates; talc; kaolin; TiO₂, SiO₂; and magnesium trisilicate, and

e) from 3 to 15 % by weight water, based on the total weight of the granulate,

V) from 0 to 60 % F of further additives from the group consisting of optical brighteners; suspending agents for dirt; pH regulators; foam regulators; salts for regulating the spray-drying and granulating properties; fragrances; antistatic agents; fabric conditioners; enzymes; bleaching agents; pigments; toning agents; polymers which, during the washing of textiles, prevent staining caused by dyes in the washing liquor which have been released from the textiles under the washing conditions; and perborate activators, and

VI) from 0 to 5 % G water.

35. A process for the preparation of a granulate according to any one of claims 1 to 29, wherein firstly an aqueous solution of the phthalocyanine compound is prepared, to which there is added the anionic dispersing agent and/or the polymer or a polymer solution, the salt and, where appropriate, further additives, and stirring is carried out until a homogeneous solution (or suspension) is obtained, and then all water, with the exception of a residual amount, is removed from the aqueous solution in a drying step, solid particles (granules) simultaneously being formed.

36. A process according to claim 35, wherein the removal of water is performed by spray-drying.

37. A process according to claim 35, wherein the removal of water is performed by spray-drying with direct return of the fines of the solid material to the spray zone.
38. A process according to claim 35, wherein the removal of water is performed in a fluidised spray-dryer.
39. A process according to claim 35, wherein the removal of water is performed in a fluidised bed granulator.
40. A process according to any one of claims 35 to 39, wherein a phthalocyanine solution purified of organic by-products by a membrane separation procedure is used.
41. A granulate as defined in any one of claims 1 to 29 with the proviso that it does not contain ethoxylated stearyl diphenyloxyethyl diethyltriamine.
42. A granulate as defined in claim 41 with the proviso that it is not encapsulated and it has a substantially homogeneous distribution of ingredients.
43. Treatment of textiles using a formulation according to any one of claims 1 to 34.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/09409

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D17/06 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 959 123 A (CIBA SC HOLDING AG) 24 November 1999 (1999-11-24) cited in the application claims 1-26 ---	1-43
A	US 5 916 481 A (WILLEY ALAN DAVID) 29 June 1999 (1999-06-29) claims 1-41 ---	1-43
A	EP 0 124 478 A (CIBA GEIGY AG) 7 November 1984 (1984-11-07) cited in the application claims 16-19 ---	1-43 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- *O* document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search

8 December 2003

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/09409

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CH 659 082 A (CIBA GEIGY AG) 31 December 1986 (1986-12-31) page 3, column 2, line 66 -page 4, column 1, line 39 page 4, column 2, line 50 - line 65 ---	1-43
A	DE 34 30 773 A (CIBA GEIGY AG) 14 March 1985 (1985-03-14) claims 1-15 ---	1-43
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A	US 4 097 418 A (ROLFES THOMAS RICHARD) 27 June 1978 (1978-06-27) claim 1; examples I,II ---	1
A	US 4 394 125 A (HOELZLE GERD ET AL) 19 July 1983 (1983-07-19) column 7, line 44 -column 8, line 33 ---	1
A	EP 0 899 325 A (CIBA GEIGY AG) 3 March 1999 (1999-03-03) claims 1-15 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/09409

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